Van der Waals Interactions in Molecules and Condensed Matter

(Including Semiconductors with Defects)

Alexandre Tkatchenko

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Berlin, Germany

IPAM MDWS1, October 4, 2012

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Van der Waals (dispersion) energy

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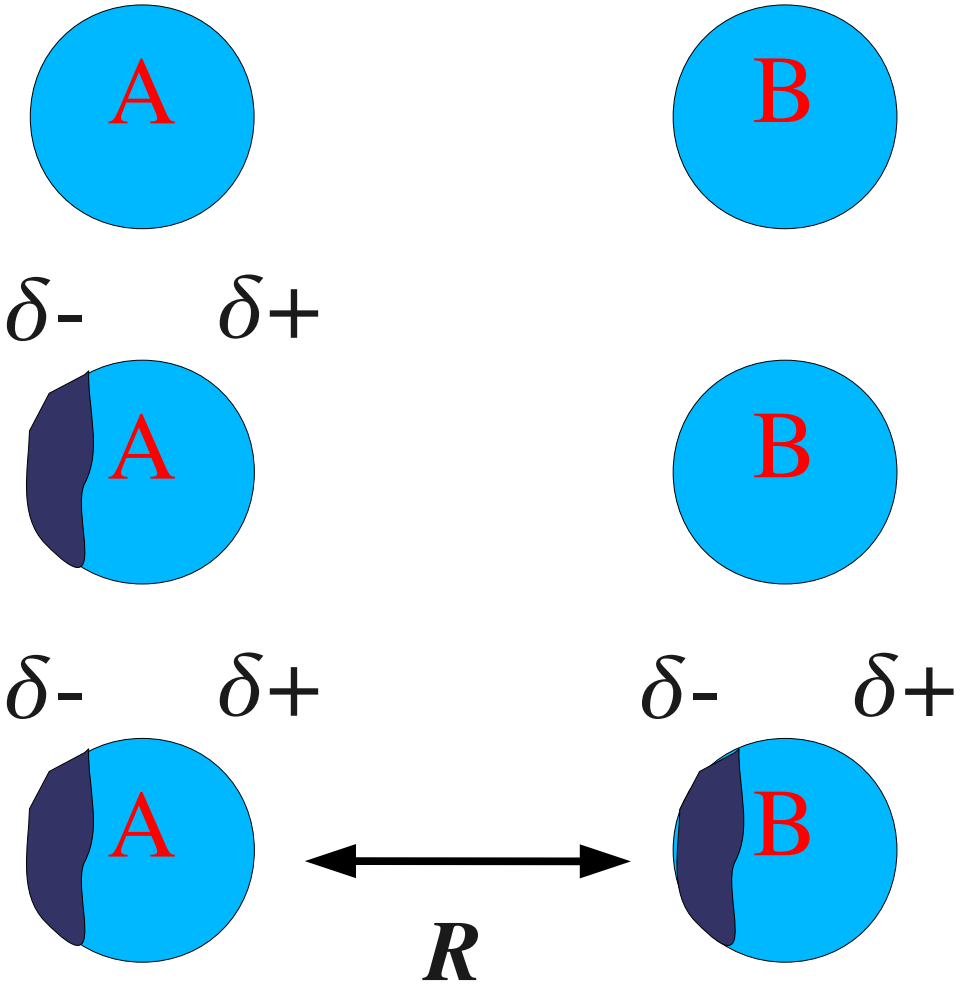

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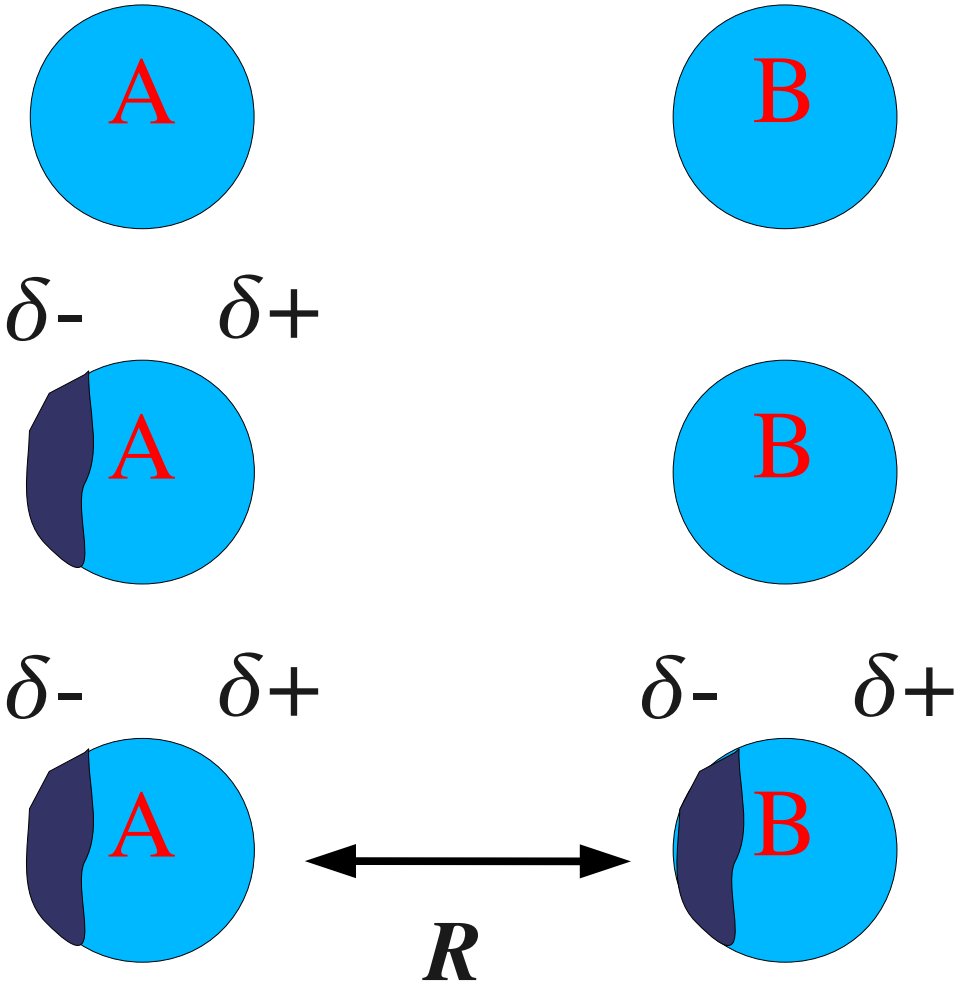

- Ubiquitous interatomic and intermolecular interaction
- Scales linearly with system size
- Weak compared to hydrogen or covalent bonds

... **but** is a significant component of *binding energies* !

$$E^{disp}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

Van der Waals Interactions: *Are They Weak?*

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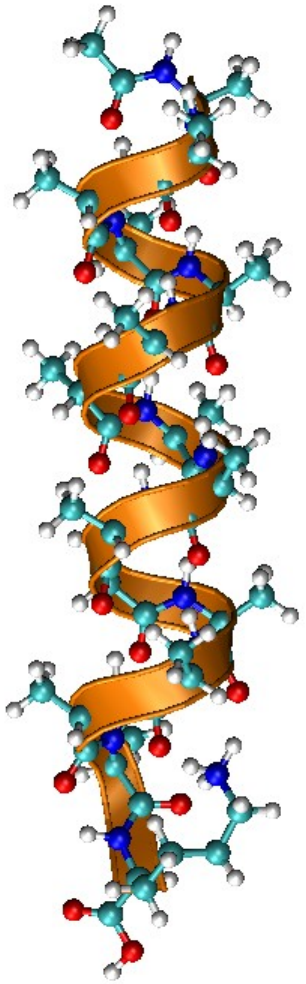

Polyalanine ($Ala_{15}LysH^{+}$) *in vacuo*

✔ Experiment predicts a stable α-helical form up to 725 K

M. F. Jarrold et al., ***J. Am. Chem. Soc.*** (1999);
J. Am. Chem. Soc. (2000).

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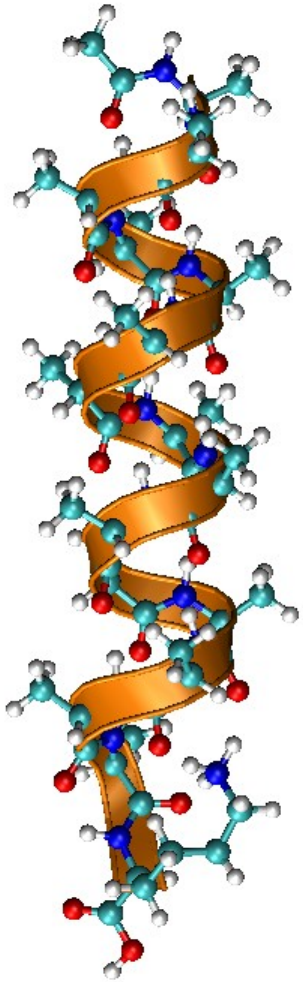

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✔ Without vdW (DFT-PBE) it converts to a 3_{10} helix at ~ 300 K

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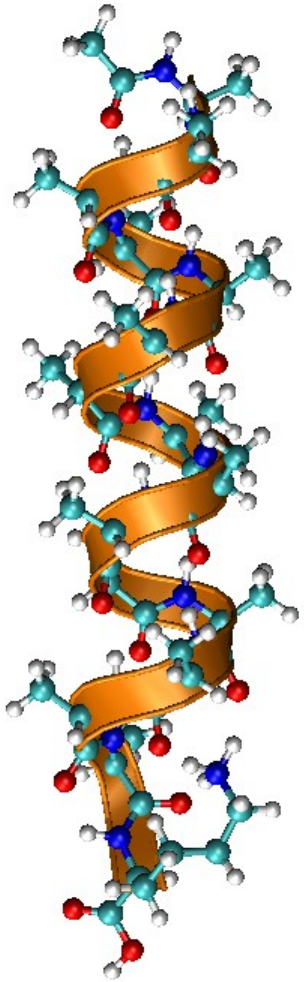

✔ Experiment predicts a stable α-helical form up to 725 K

✔ Without vdW (DFT-PBE) it converts to a 3_{10} helix at ~ 300 K

✔ With vdW (DFT-PBE+vdW) the α-helical-like form is stable up to 700 K, in agreement with experiment

✔ The vdW energy contributes ~ 7 kcal/mol (0.3 eV) per residue!

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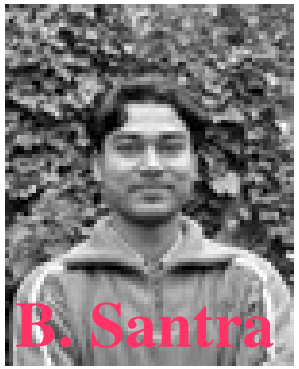
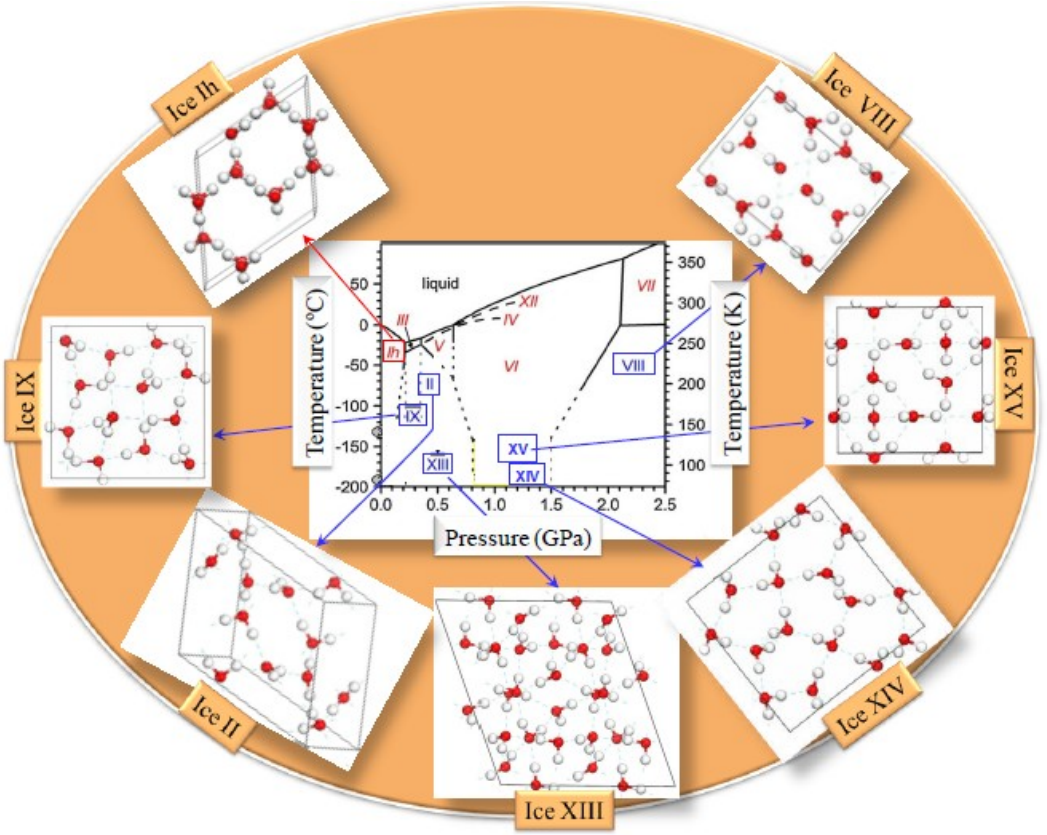
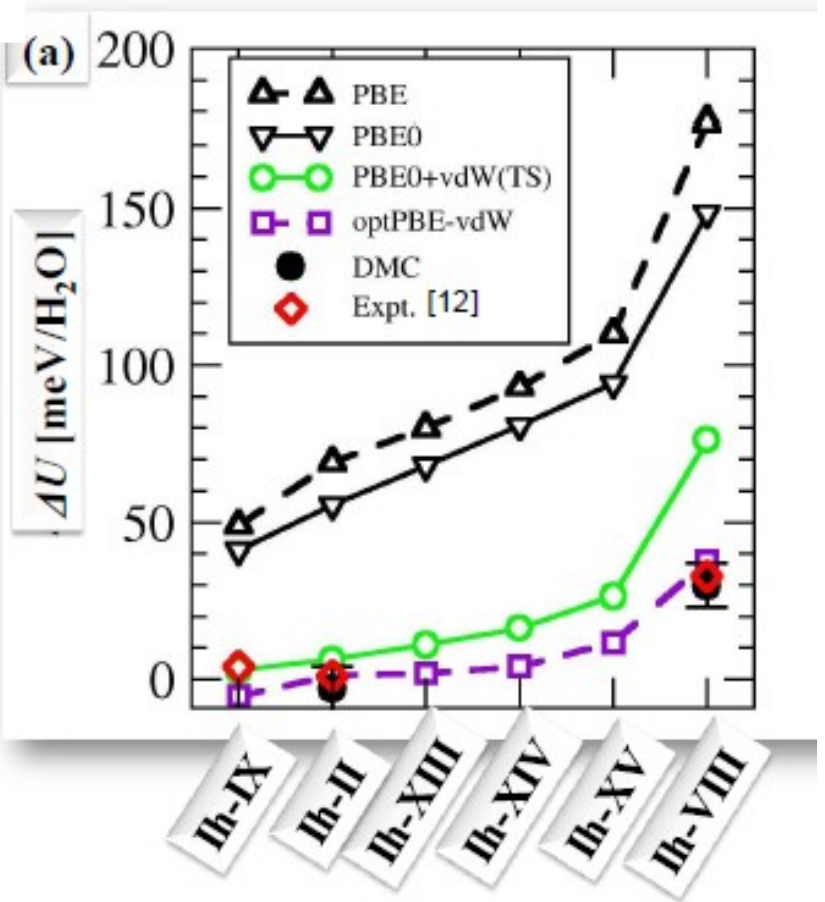


Van der Waals Interactions: *Are They Weak?*

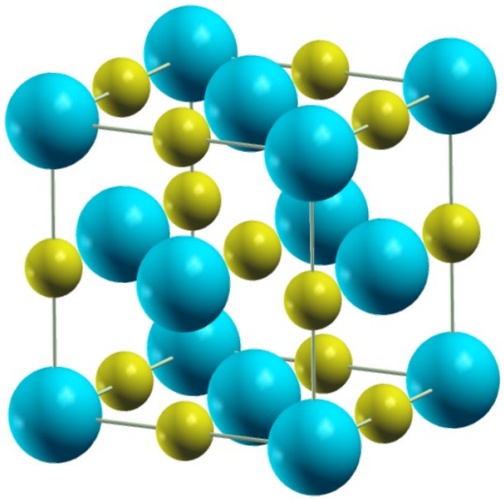
Ice at ambient and high pressures

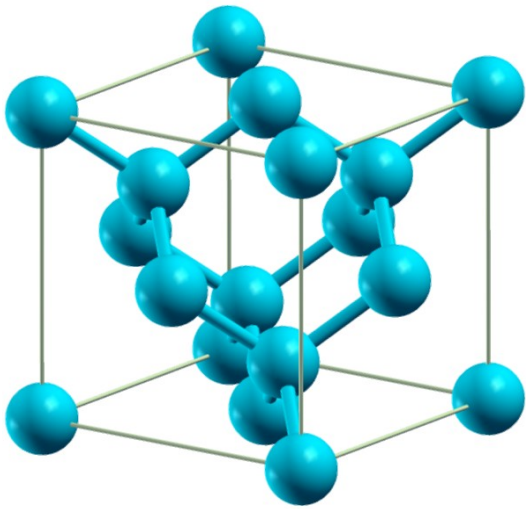




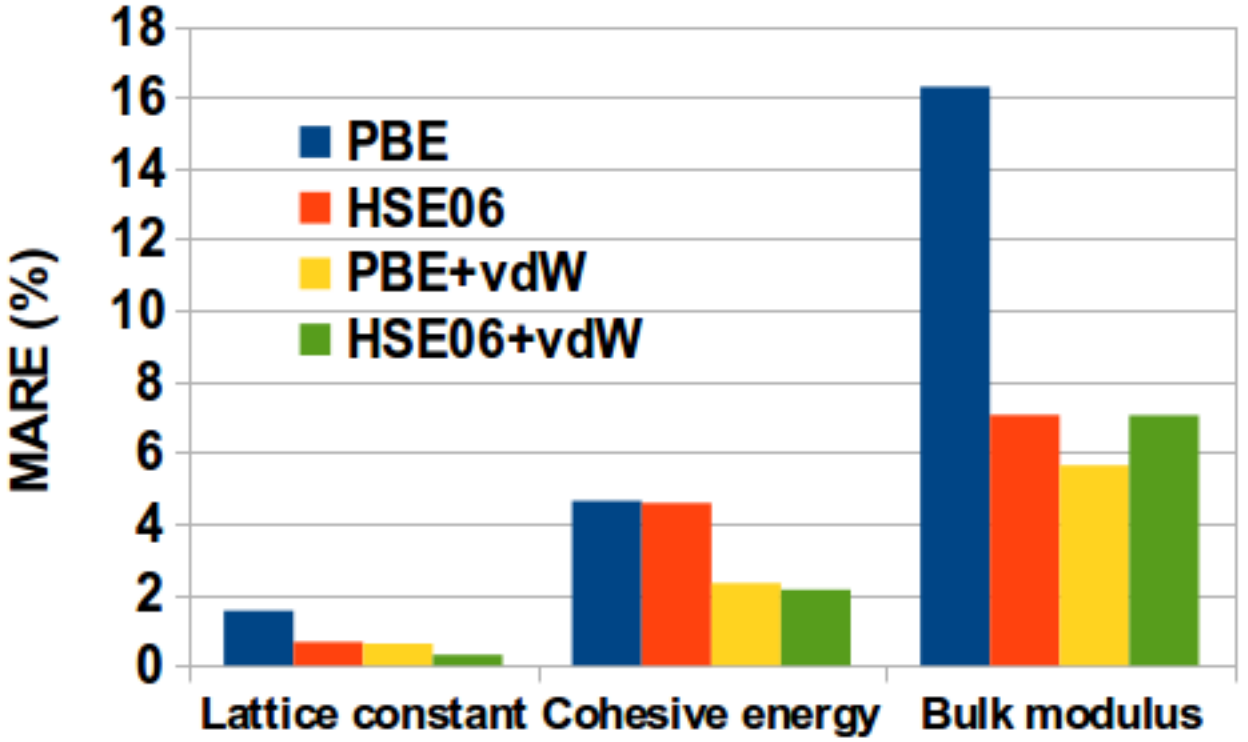
B. Santra, J. Klimes, D. Alfe, A. Tkatchenko, B. Slater, A. Michaelides, R. Car, M. Scheffler, ***Phys. Rev. Lett.*** (2011).

Van der Waals Interactions: *Are They Weak?*





Semiconductors and ionic solids

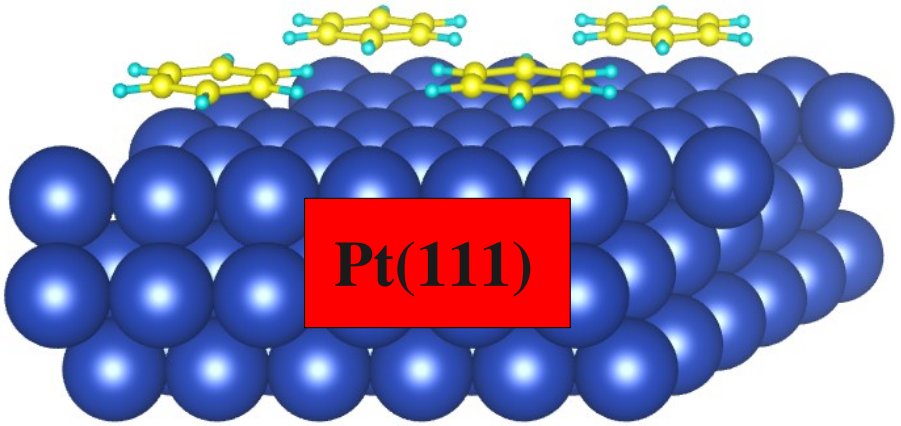


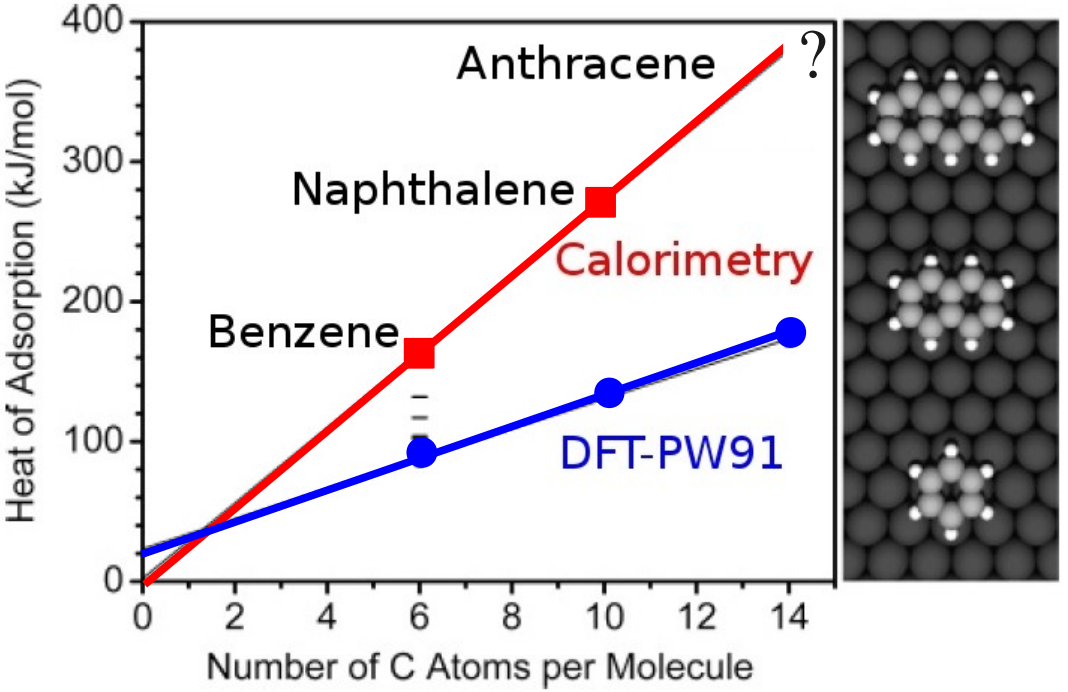
The vdW energy contributes 0.2-0.3 eV/atom to the cohesive energy, 3-17 GPa to the bulk modulus, and 0.01-0.15 A to the lattice constant

G.-X. Zhang, A. Tkatchenko, J. Paier, H. Appel, M. Scheffler, ***Phys. Rev. Lett.*** (2011).

Van der Waals Interactions: *Are They Weak?*

Are van der Waals interactions important for chemisorption ?





Gottfried et al., ***J. Phys. Chem. B*** 110, 17359 (2006).

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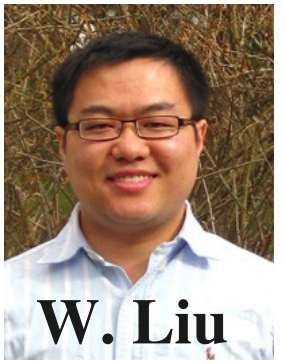
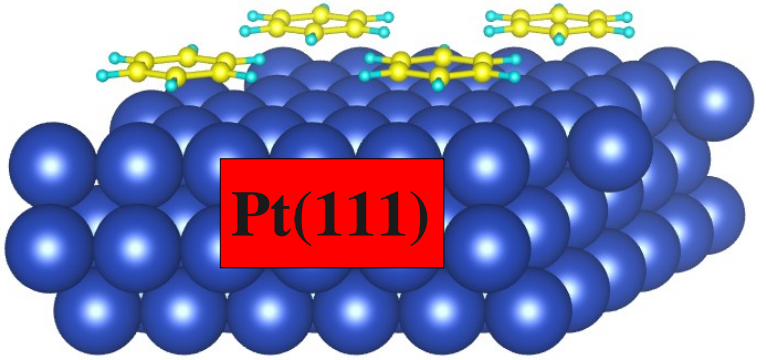
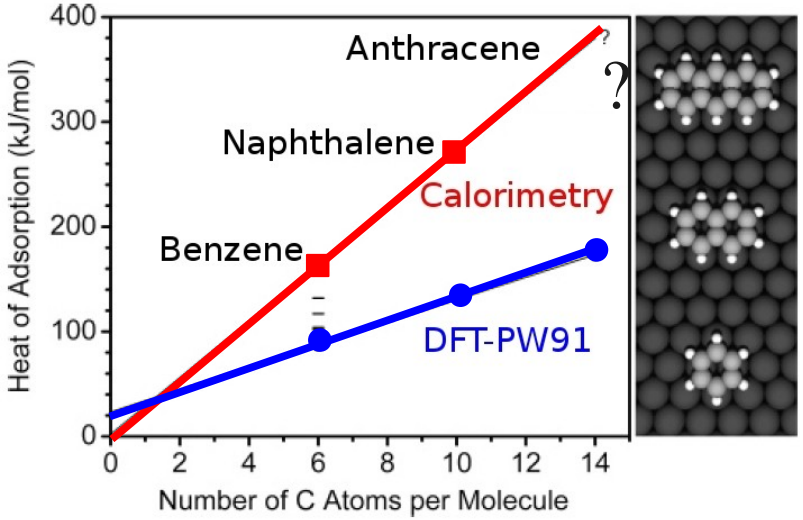
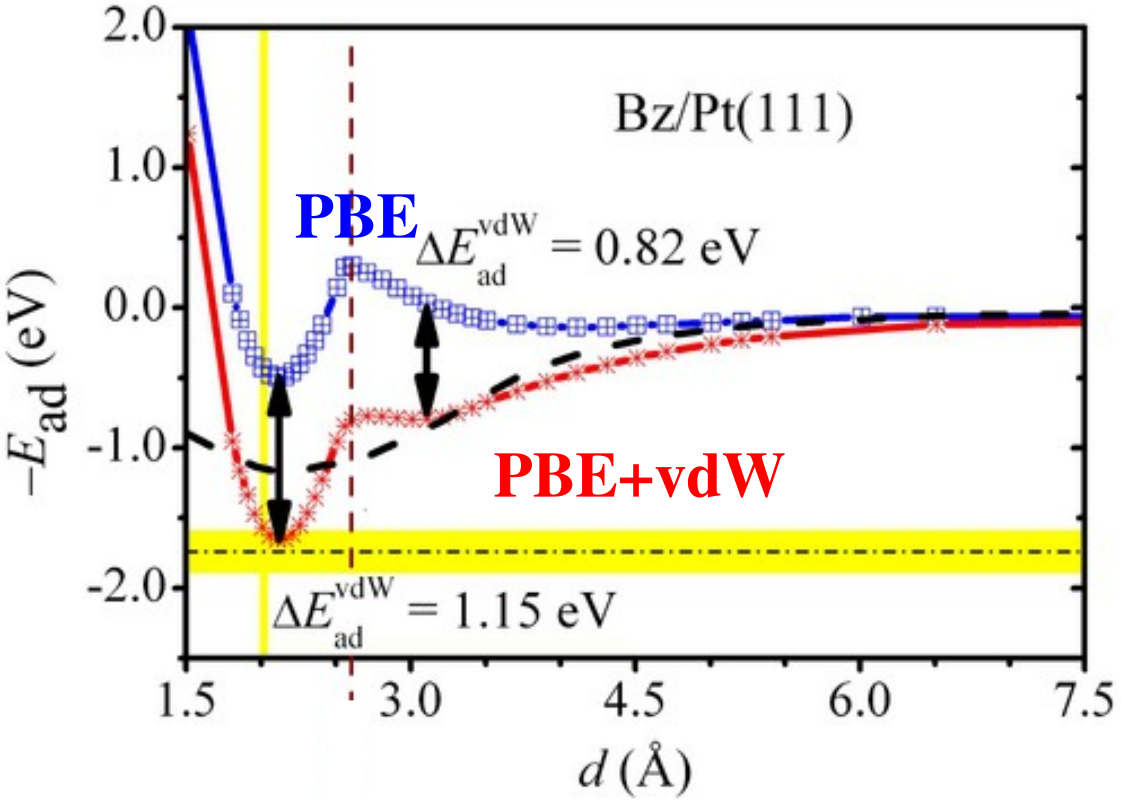


Van der Waals interactions are crucial *even* for chemisorption



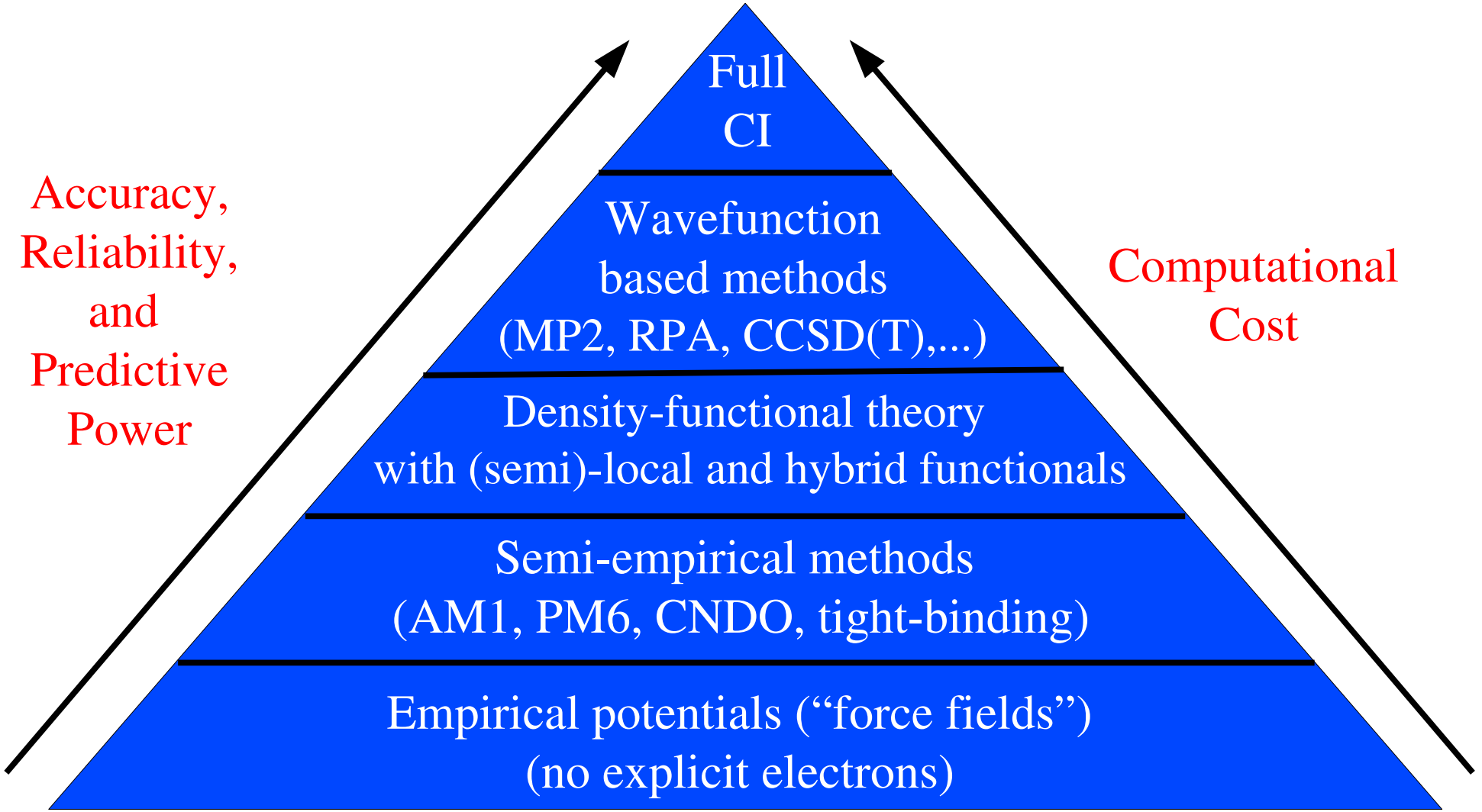




V. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, ***Phys. Rev. Lett.*** (2012);
W. Liu et al., ***Phys. Rev. Lett.***, submitted (2012).

Current state-of-the-art of atomistic modeling

$$H\Psi = E\Psi$$



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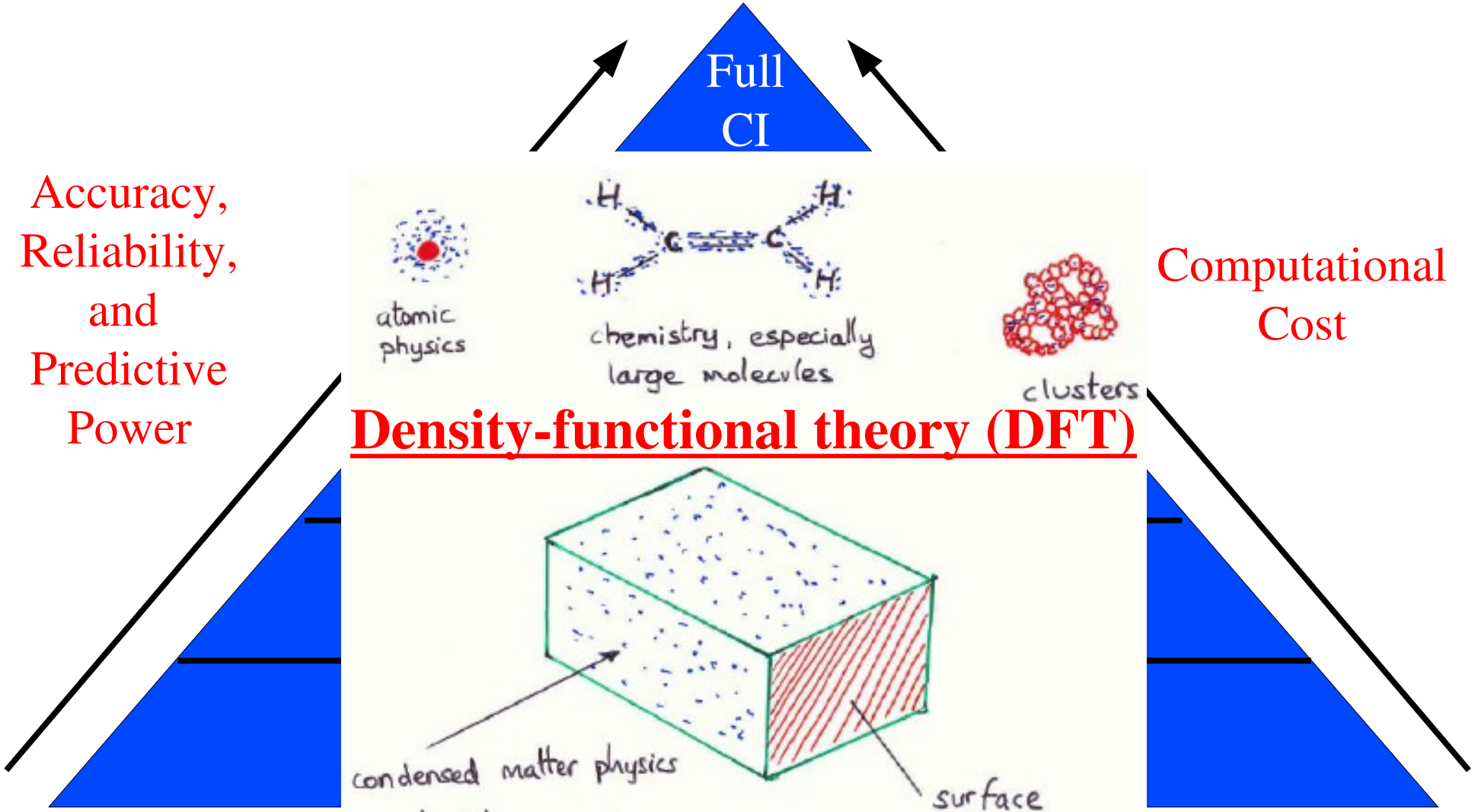
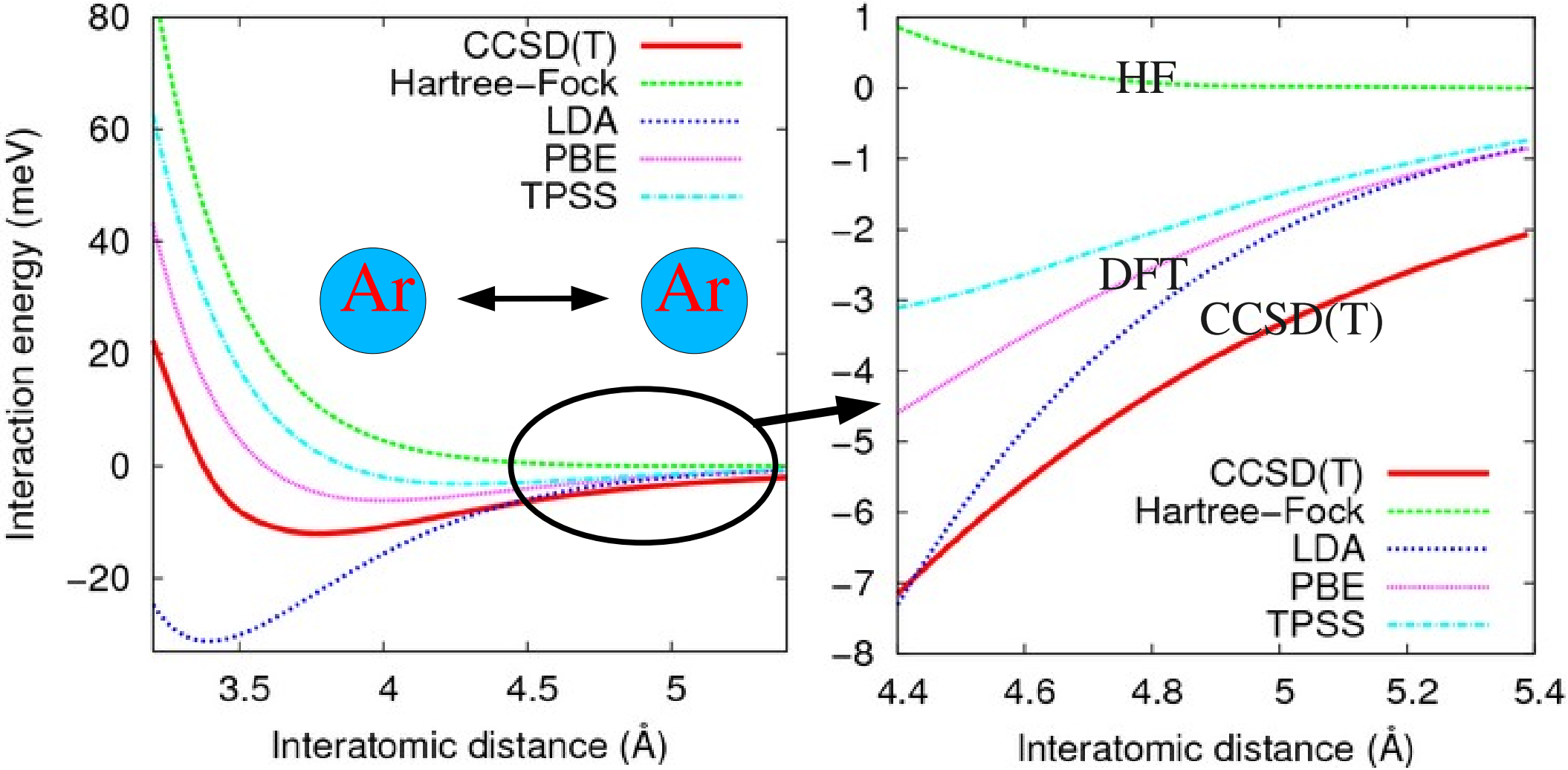


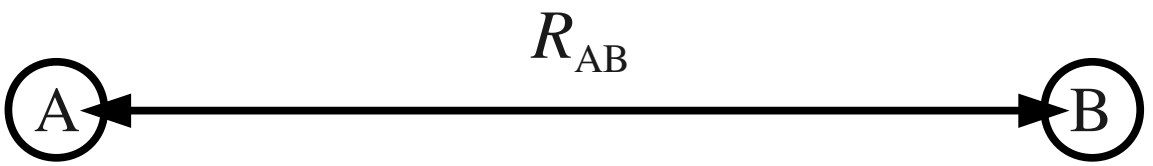
K. Burke, IPAM, 2011

DFT and vdW interaction: Rare-gas dimers

$$E^{disp}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$



Accurate *First-Principles* Modeling of vdW Interactions is Challenging



$$E_{\mathrm{vdW}}^{(2)} = -\frac{C_6^{\mathrm{AB}}}{R_{\mathrm{AB}}^6} \quad \rightarrow \quad C_6^{\mathrm{AB}} = \frac{3}{\pi}\int \alpha_{\mathrm{A}}(i\omega)\alpha_{\mathrm{B}}(i\omega)d\omega$$

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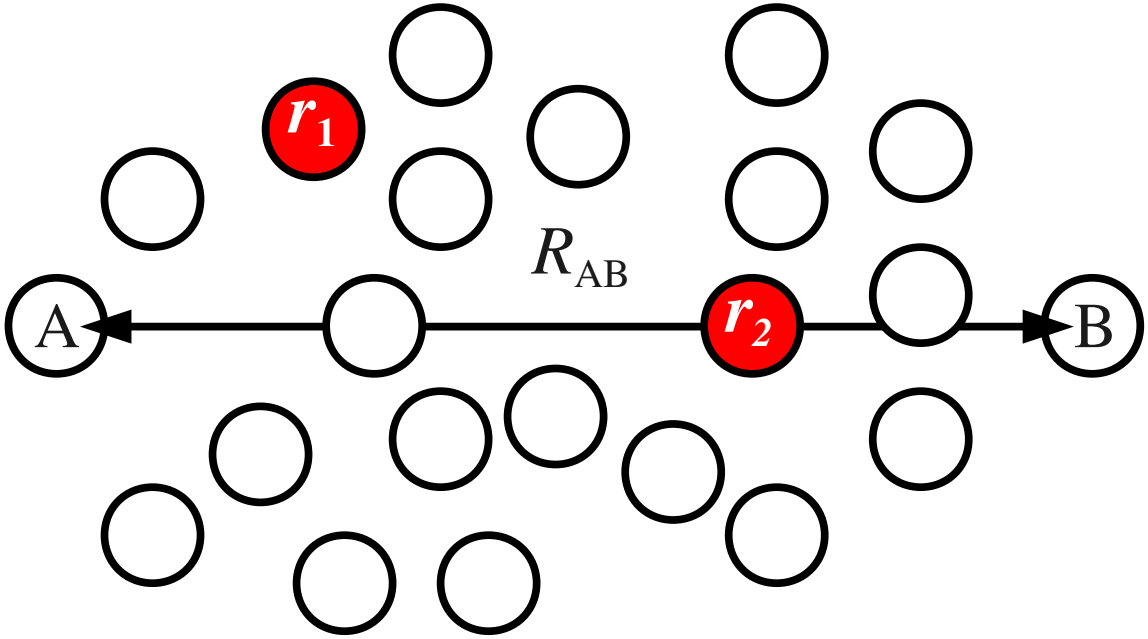

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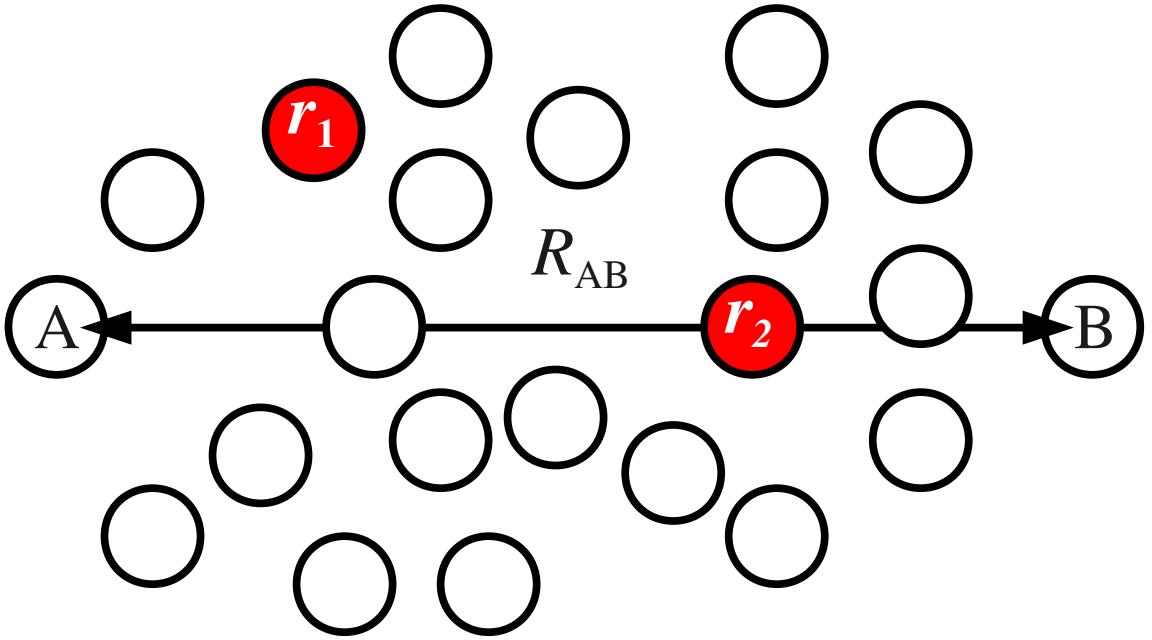

$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

ACFDT: Adiabatic connection fluctuation-dissipation theorem

O. Gunnarsson and B. I. Lundqvist, ***Phys. Rev. B*** (1976);

D. C. Langreth and J. P. Perdew, ***Phys. Rev. B*** (1977).

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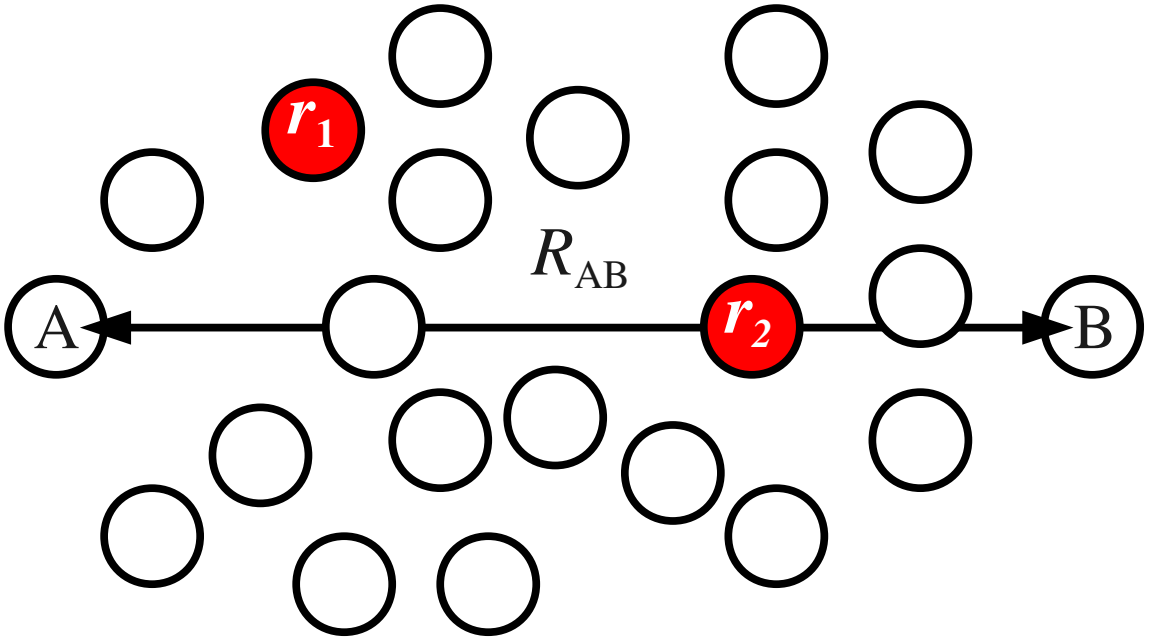

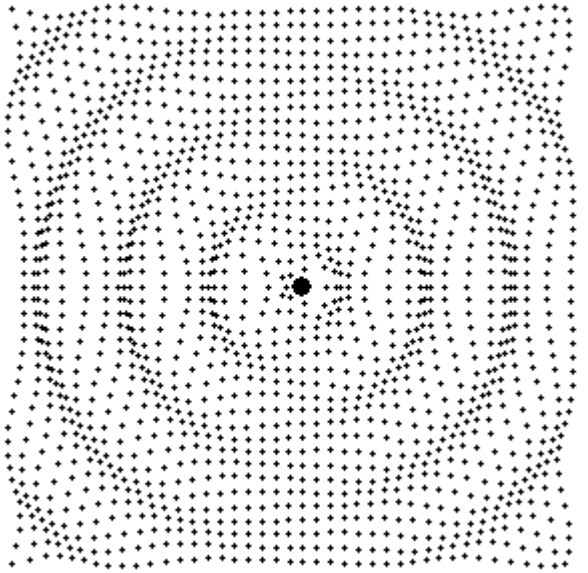

http://www.acs.psu.edu/drussell/Demos/forkanim/forkanim.html

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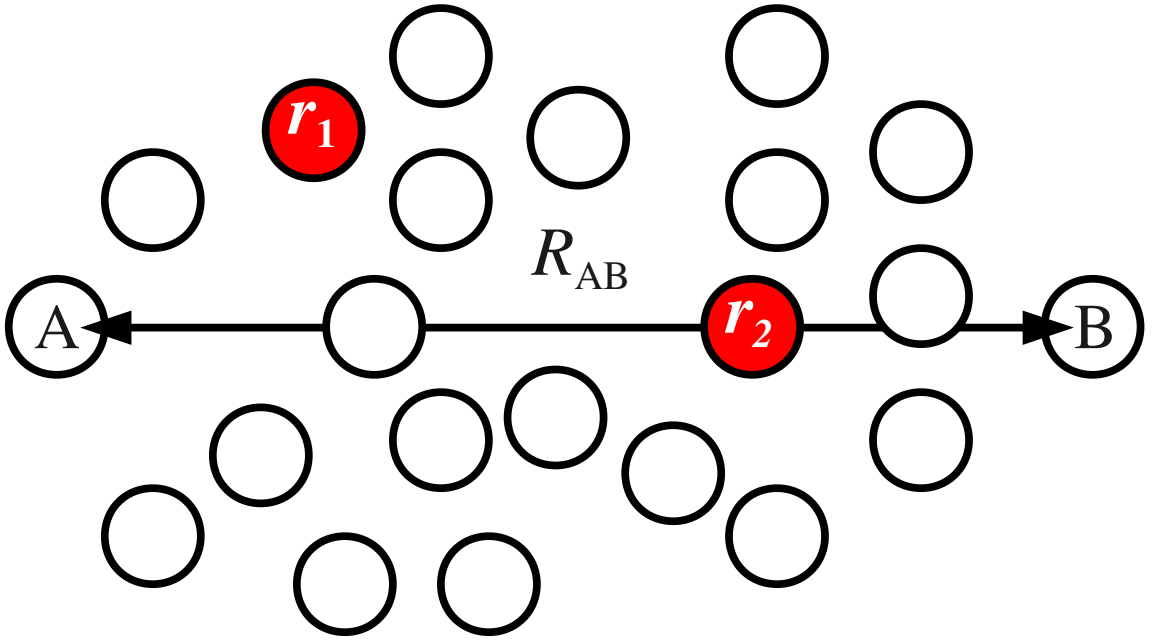
Accurate *First-Principles* Modeling of vdW Interactions is Challenging

1

Accurate Microscopic Modeling of Coulomb Screening



2

Full (All-Order) Many-Body van der Waals Energy

$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

(Approximate) concepts and methods for dispersion in DFT

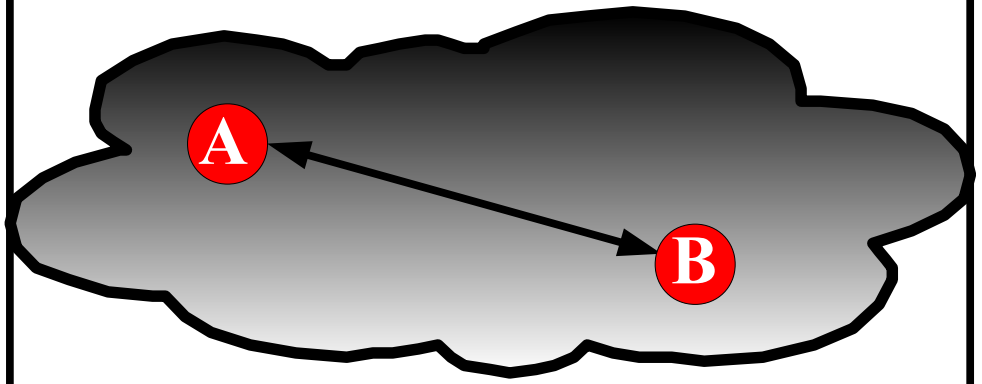
$$E_{\rm xc} = E_{ex}^{\rm GGA\ or\ EX} + E_{\rm corr}^{\rm LDA,GGA} + E_{\rm corr}^{\rm non-local}$$

- Non-local functionals (depend explicitly on ***r*** and ***r'***) (*Langreth, Lundqvist et al.*).
- Modified pseudopotentials (*von Lilienfeld et al.*)
- Highly empirical (hybrid) meta-GGA functionals (*Truhlar et al.*)
- Interatomic (pairwise or beyond) dispersion corrections (Many people)

Wu and Yang ***JCP*** *(2002);* *Grimme* ***J. Comp. Chem.*** (2004,2006); *Dion et al.* ***PRL*** (2004); *Zhao and Truhlar* ***JCP*** (2006); *von Lilienfeld et al.* ***PRL*** (2004); *Johnson and Becke* ***JCP*** (2005-2007); *Tkatchenko and Scheffler* ***PRL*** (2009); and many others ...

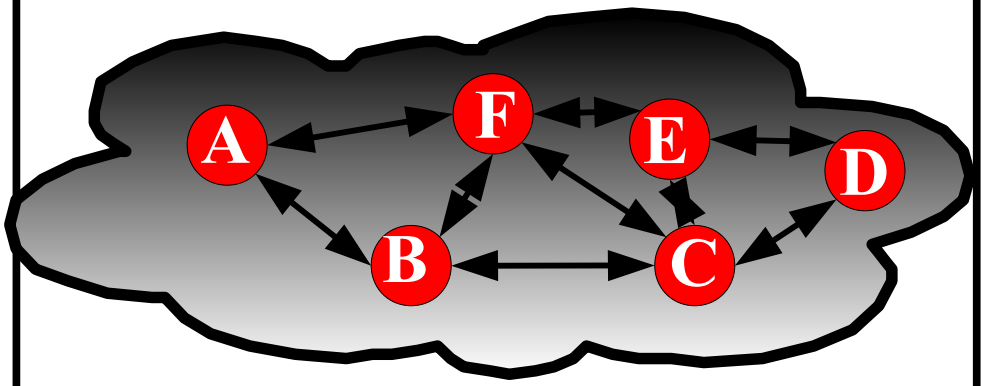
Towards Efficient Many-Body Treatment of vdW Interactions

The current state-of-the-art (*Grimme, Becke, Tkatchenko/Scheffler, Langreth/Lundqvist, ...*):
Effective screening and two-body energy



Valid for
small molecules ***or***
homogeneous dielectrics

The new state-of-the-art:
Full many-body screening and energy for a system of quantum oscillators



Valid for small and large molecules, insulators, metals, interfaces, ...

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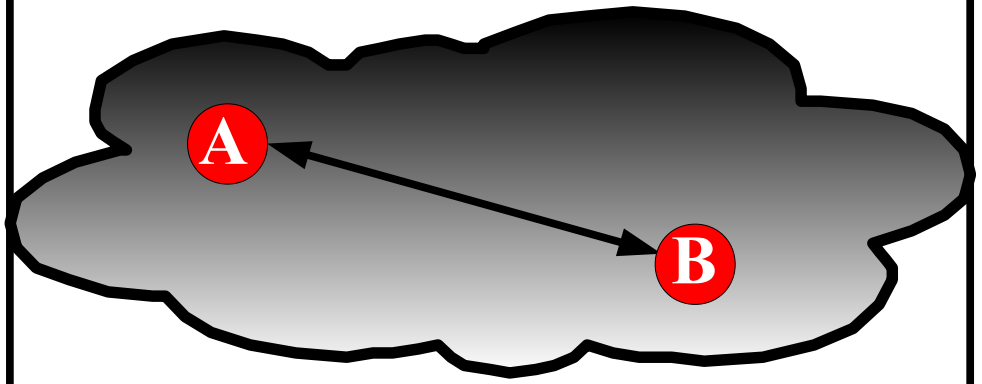

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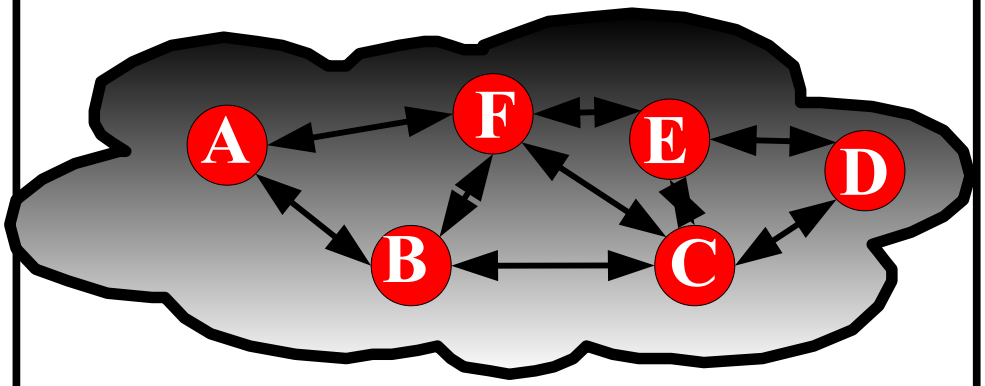

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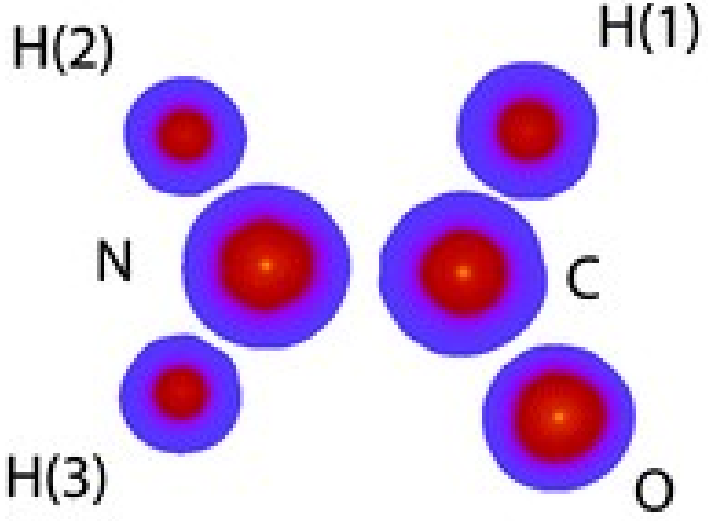
* *A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler*, ***Phys. Rev. Lett.*** (2012).
Related work: *B. J. Berne, G. Martyna, A. Donchev, M. W. Cole, K. Jordan, et al.*

TS-vdW method: Atomic vdW parameters from first principles



$$\alpha_A^0 = \alpha_A^0[n(\mathbf{r})]; \quad \omega_A^0 = \omega_A^0[n(\mathbf{r})]$$

$$\alpha_A(i\omega) = \frac{\alpha_A^0}{1 + (\omega/\omega_A^0)^2}$$

$\boldsymbol{\alpha}^0$ and $\boldsymbol{\omega}^0$ include short-range screening

A. Tkatchenko and M. Scheffler, ***Phys. Rev. Lett.*** (2009)

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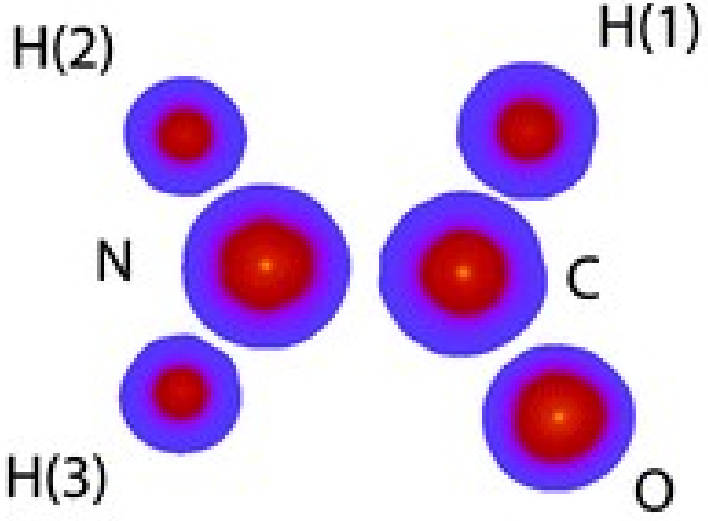

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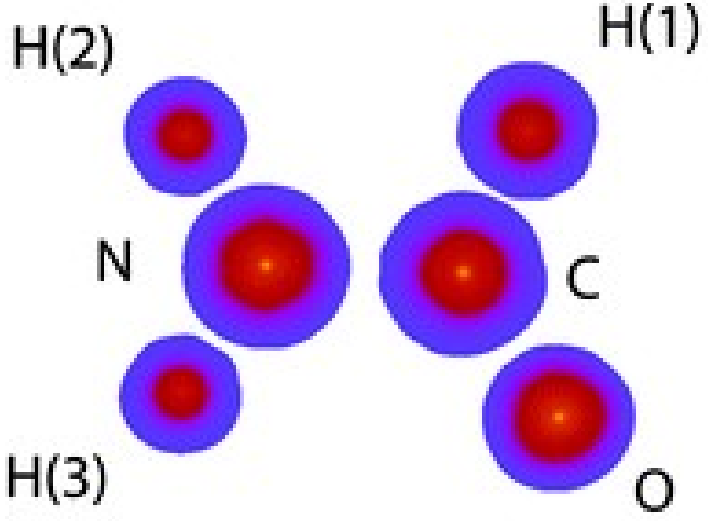

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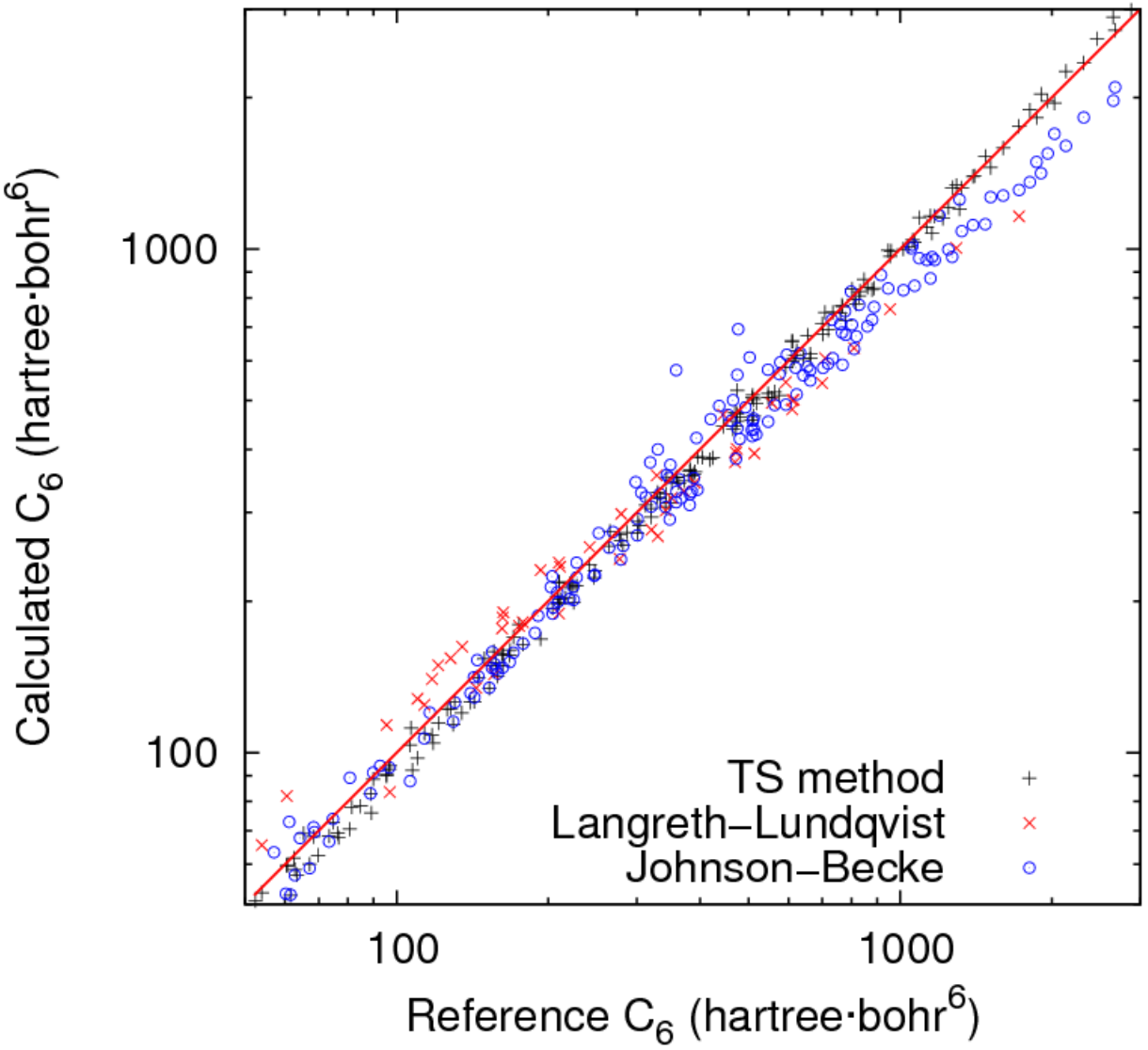
Only 1 training parameter coupling DFT and vdW:
scaling of the vdW radius

A. Tkatchenko and M. Scheffler, ***Phys. Rev. Lett.*** (2009)

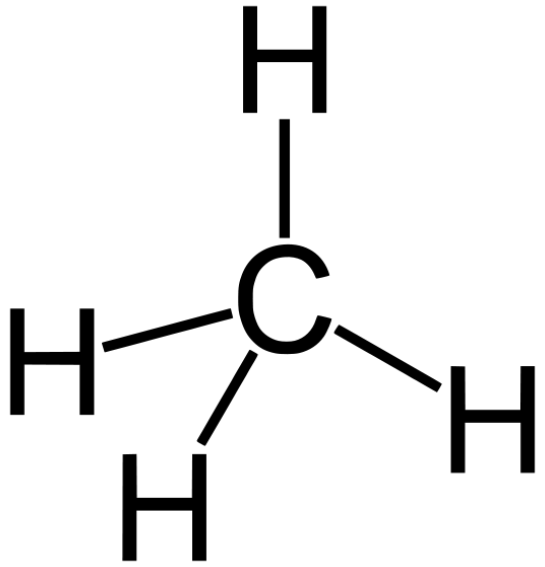
Performance of TS-vdW method for molecules



Mean absolute error of 5.5% for 1225 molecular C_6 from reference DOSD data of *W. J. Meath et al.*

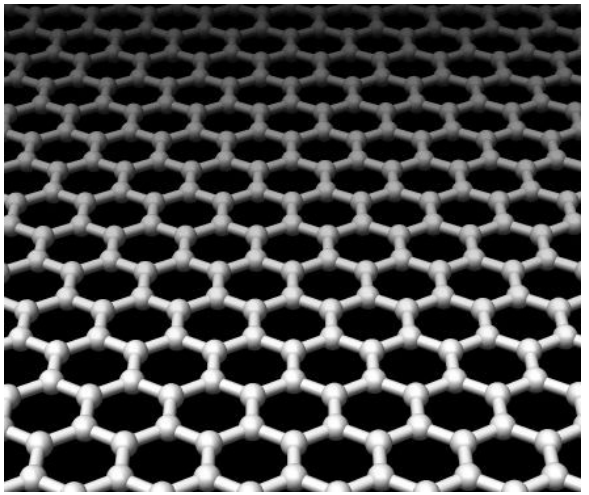
C_6 is a functional of the electron density

(Carbon-Carbon C_6 coefficient / HartreeBohr^6)



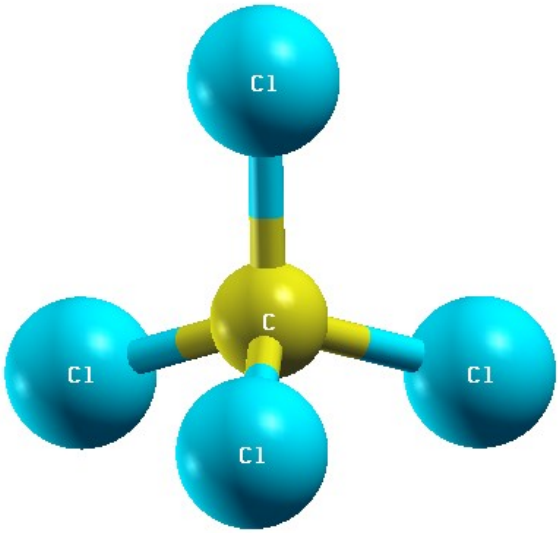
24.1

sp^3



33.0

sp^2



43.1

sp^3

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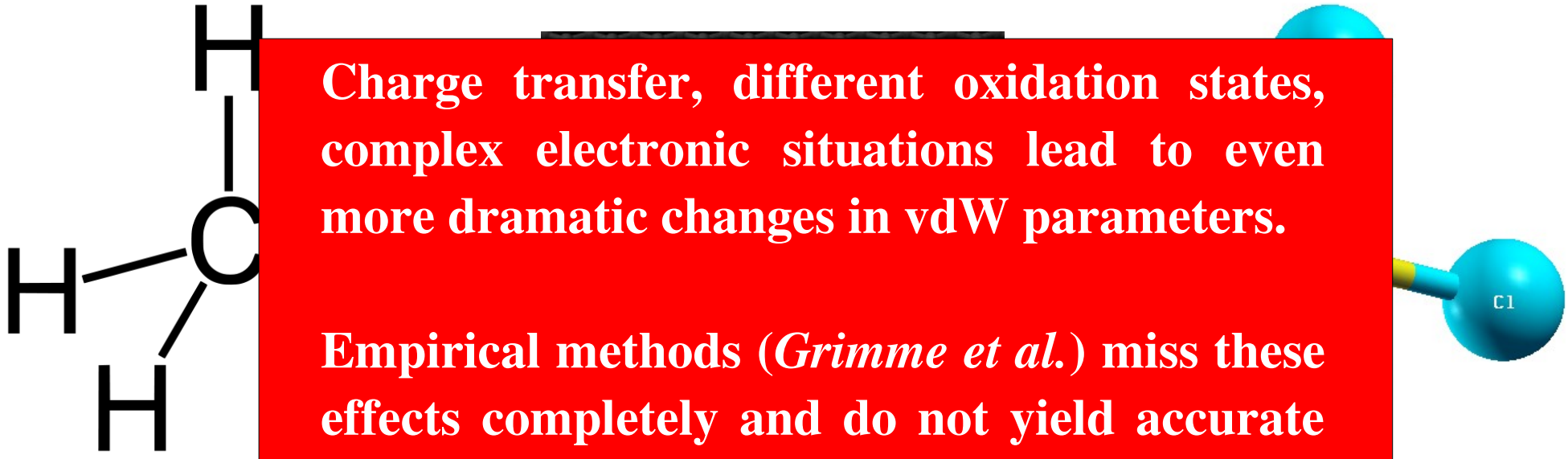


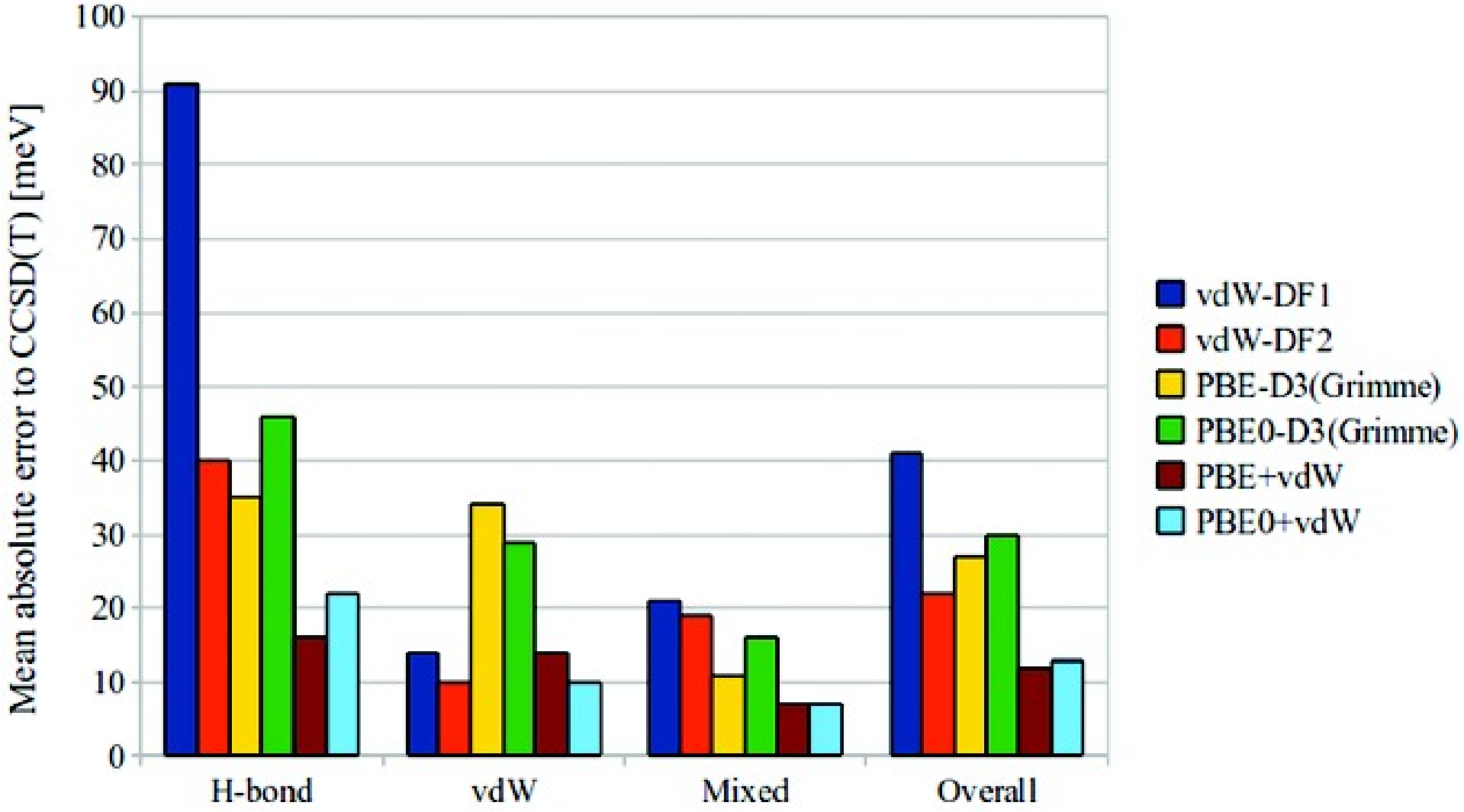
Charge transfer, different oxidation states, complex electronic situations lead to even more dramatic changes in vdW parameters.

Empirical methods (*Grimme et al.*) miss these effects completely and do not yield accurate vdW energies.

24.1

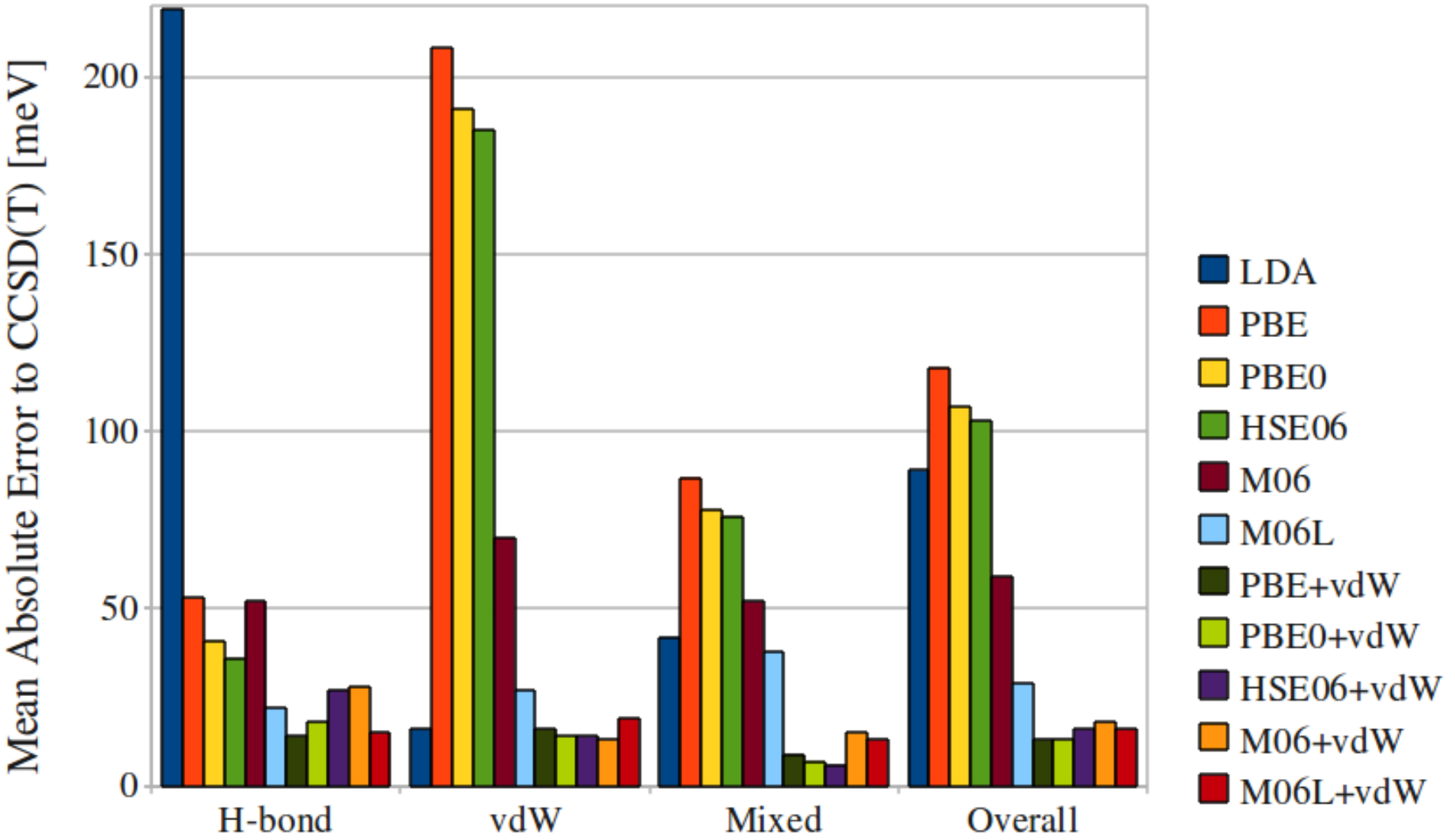
sp^3 sp^2 sp^3

Performance of TS-vdW method for intermolecular interactions



CCSD(T) reference interaction energies: *D. Sherrill et al.*, ***JCP*** (2011).

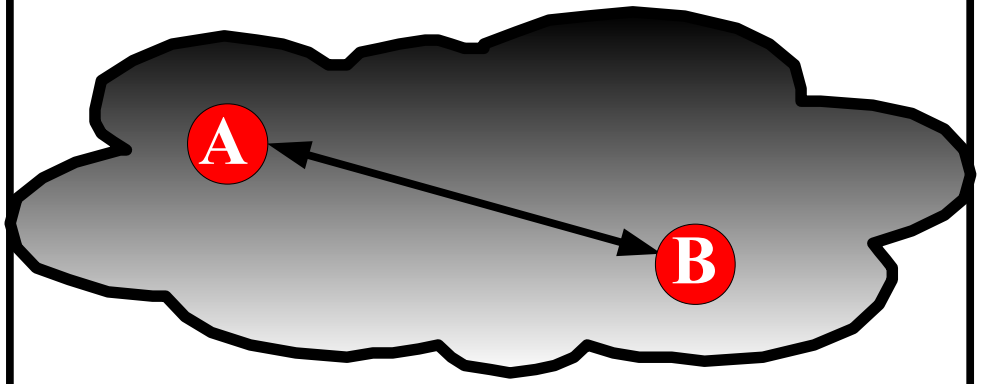
Performance of TS-vdW method with different DFT functionals



N. Marom, A. Tkatchenko et al. ***JCTC*** (2011).

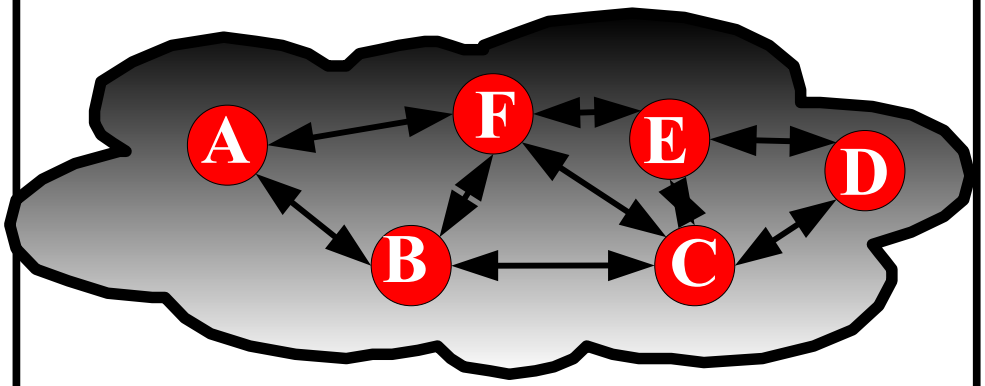
Towards Efficient Many-Body Treatment of vdW Interactions

The current state-of-the-art (*Grimme, Becke, Tkatchenko/Scheffler, Langreth/Lundqvist, ...*):
Effective screening and two-body energy



Valid for
small molecules ***or***
homogeneous dielectrics

The new state-of-the-art:
Full many-body screening and energy for a system of quantum oscillators*

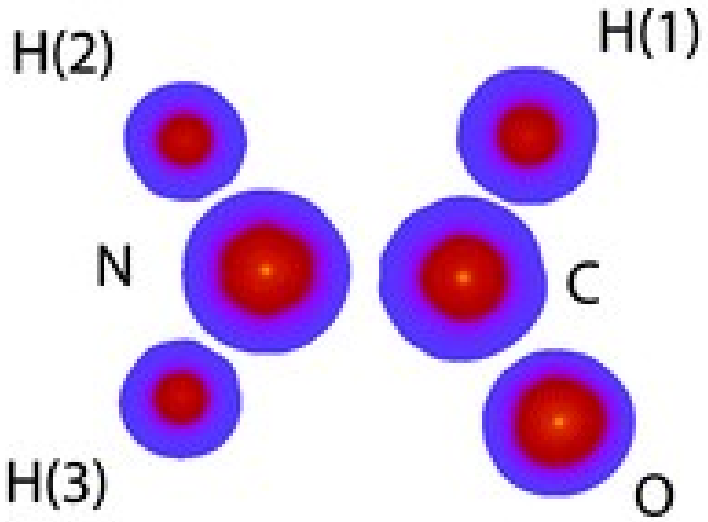


Valid for **small and large molecules, insulators, metals, interfaces, ...**

* *A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler*, ***Phys. Rev. Lett.*** (2012).
Related work: *B. J. Berne, G. Martyna, A. Donchev, M. W. Cole, K. Jordan, et al.*

Building up on the TS-vdW method: Quantum harmonic oscillators

$$\alpha_A^0 = \alpha_A^0[n(\mathbf{r})]; \quad \omega_A^0 = \omega_A^0[n(\mathbf{r})]$$



$$\alpha_A(i\omega) = \frac{\alpha_A^0}{1 + (\omega/\omega_A^0)^2}$$

Polarizability corresponds to a Quantum Harmonic Oscillator (QHO)

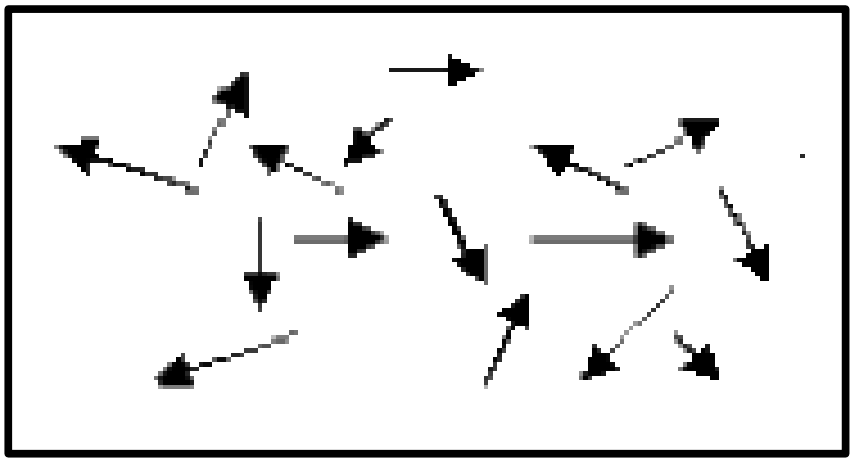
$$n[\mathbf{r}] = \frac{1}{\pi^{3/2}\mu^3} \exp\left(-r^2/\mu^2\right)$$

A. Tkatchenko and M. Scheffler, ***PRL*** (2009)

Coupled-dipole model: Self-consistent electrostatic screening (SCS)

From TS-vdW method

$$\alpha(\mathbf{r};\omega) = \alpha_0(\mathbf{r};\omega) + \alpha_0(\mathbf{r};\omega) \int d\mathbf{r}' \mathcal{T}(\mathbf{r}-\mathbf{r}')\alpha(\mathbf{r}';\omega)$$



Silberstein, Applequist, Thole, Swart, Mayer, et al.

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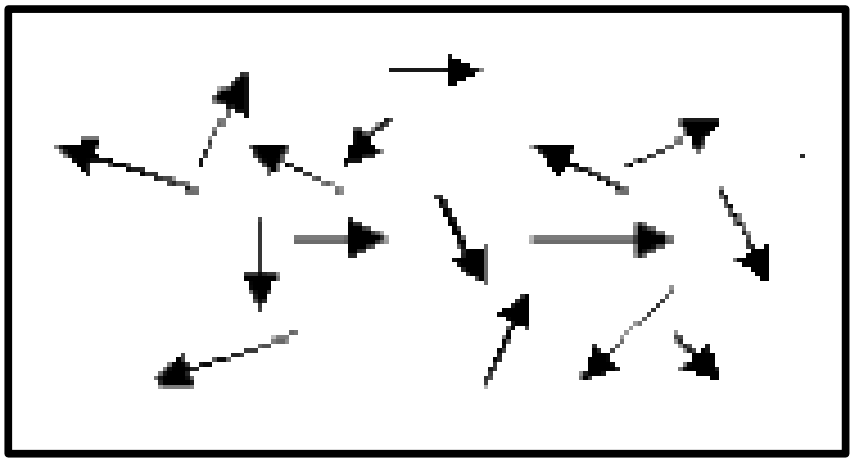
$$\alpha(\mathbf{r};\omega) = \alpha_0(\mathbf{r};\omega) + \alpha_0(\mathbf{r};\omega)\int d\mathbf{r}'\mathcal{T}(\mathbf{r}-\mathbf{r}')\alpha(\mathbf{r}';\omega)$$

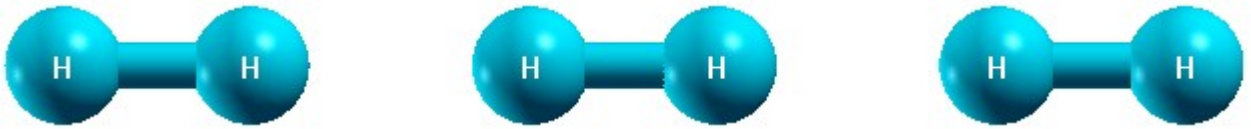
$$\alpha_p(i\omega) = \alpha_p^{\mathrm{TS}}(i\omega) + \alpha_p^{\mathrm{TS}}(i\omega)\sum_{q\neq p}^{N}\mathcal{T}_{pq}\alpha_q(i\omega)$$

Short-range modified dipole-dipole interaction tensor (QHO--QHO)



Silberstein, Applequist, Thole, Swart, Mayer, et al.

SCS: Polarization and anisotropy in H_6

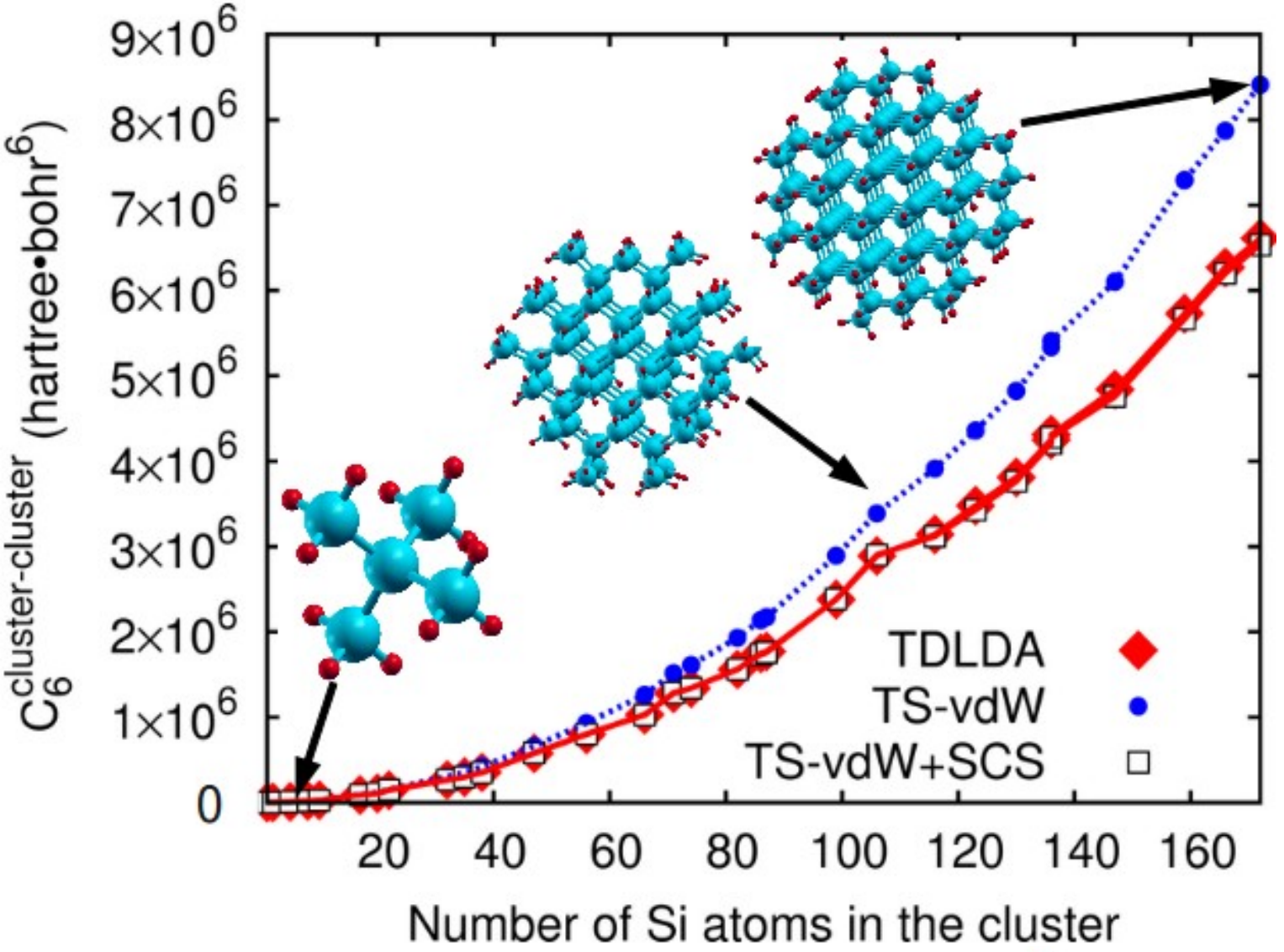


	$C_{6\perp}$	$C_{6\parallel}$	C_6^{iso}	
TS-vdW:	166	161	165	
+SCS:	89	692	223	
LR-CCSD:	115	638	238	(Reference)

$$C_6^{AA} = \frac{3}{\pi}\int [\alpha_A(i\omega)]^2 d\omega$$

All values in HartreeBohr^6

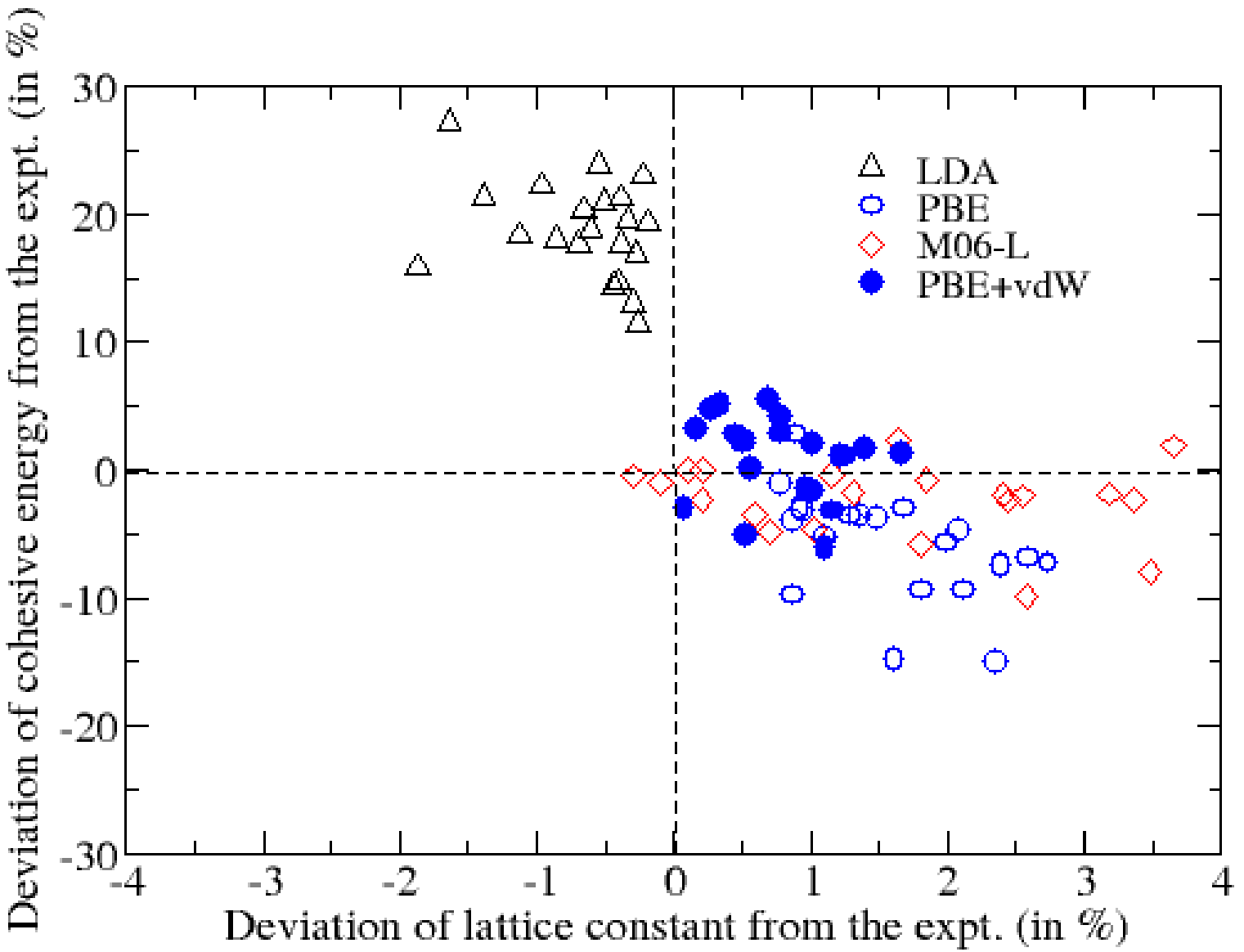
SCS: *Depolarization* in silicon clusters



TDLDA: *S. Botti et al.*, ***PRB*** (2008)

$$C_6^{AA} = \frac{3}{\pi} \int [\alpha_A(i\omega)]^2 d\omega$$

Van der Waals interactions in defect-free semiconductors



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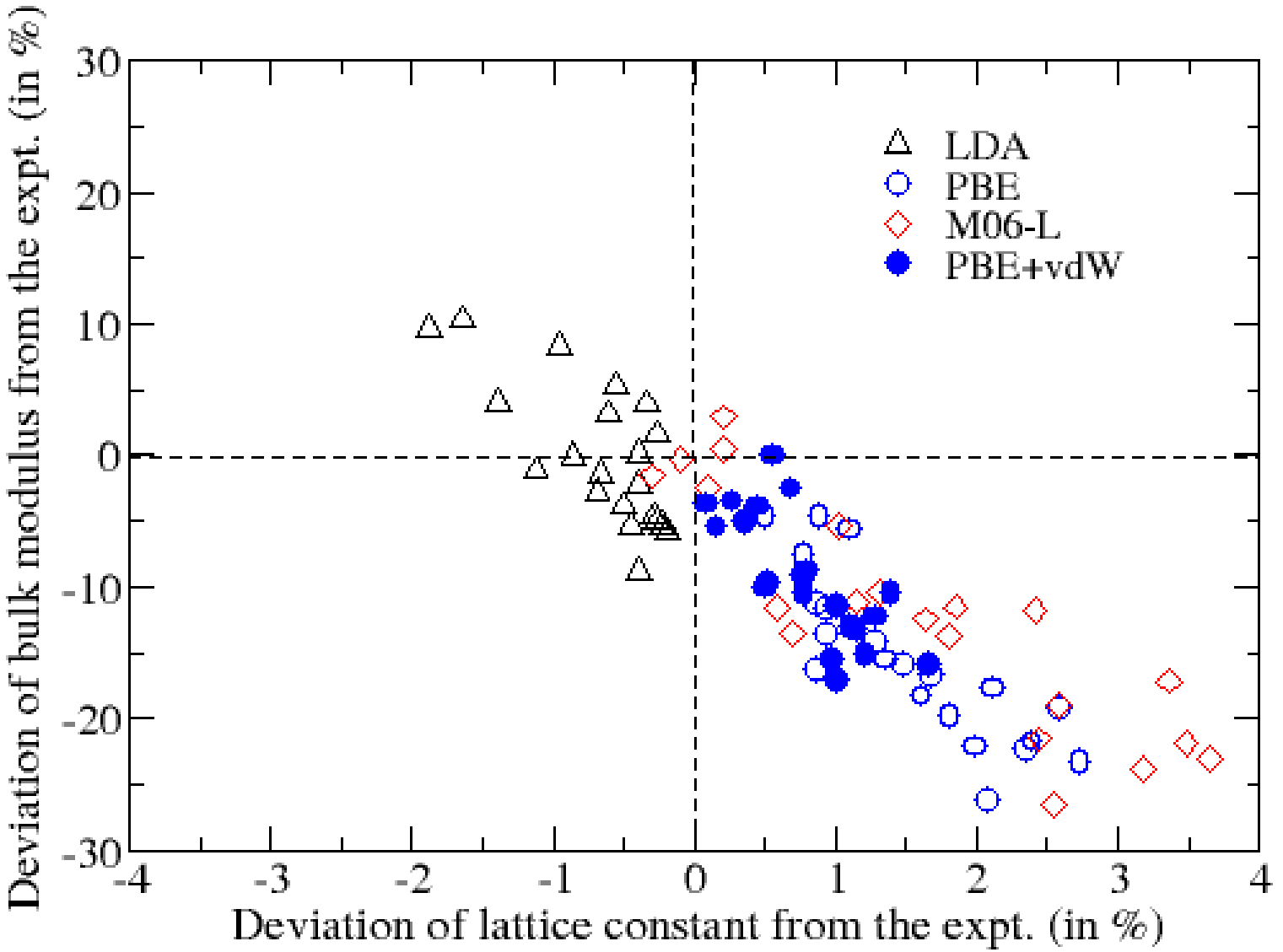
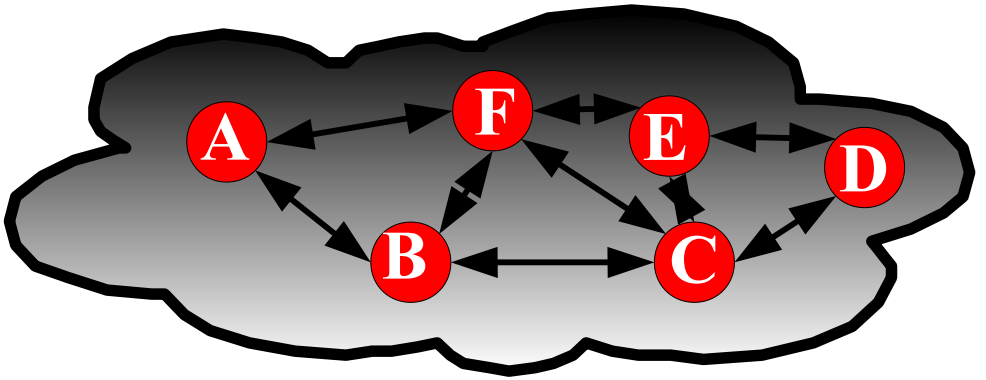


Defects in semiconductors: Important test systems for vdW

Defects have a significant effect on optical and electrical properties of semiconductors

Van der Waals interactions are intimately related to optical response



Defects in semiconductors: Important test systems for vdW

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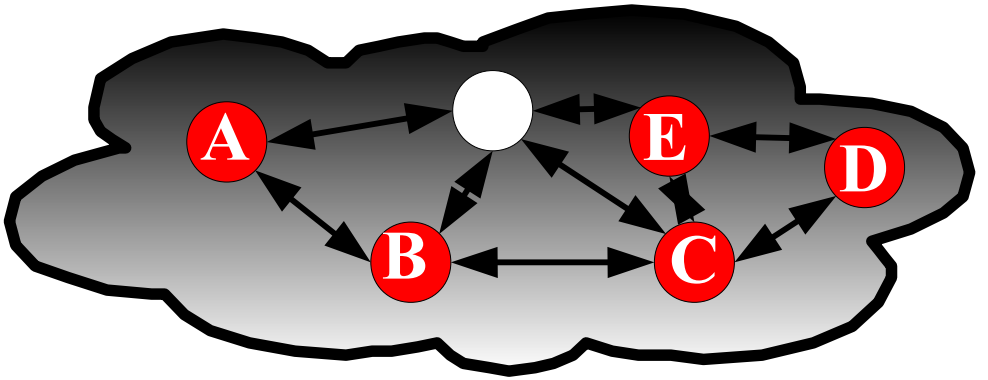
Modification of (dynamic) electric fields. What is the effect of vdW interactions?



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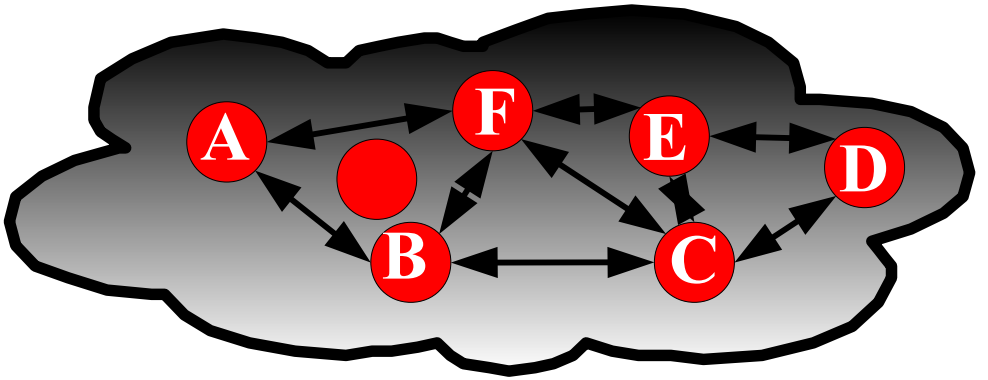
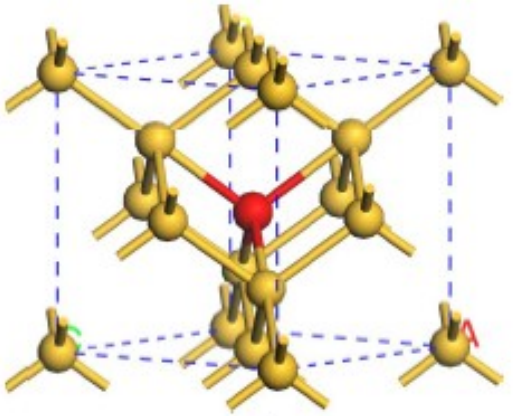
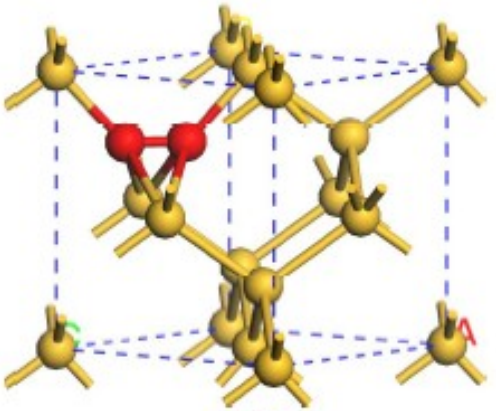


Formation energy of point defects in silicon: vdW energy contribution

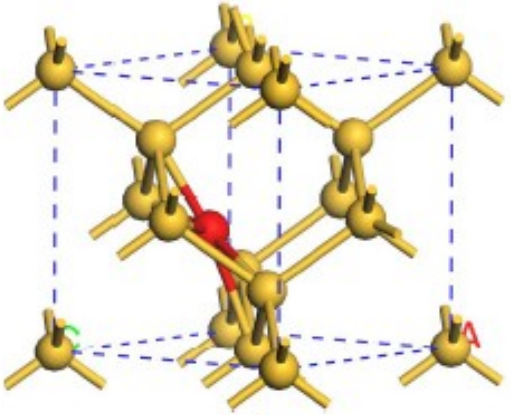
-0.20 eV

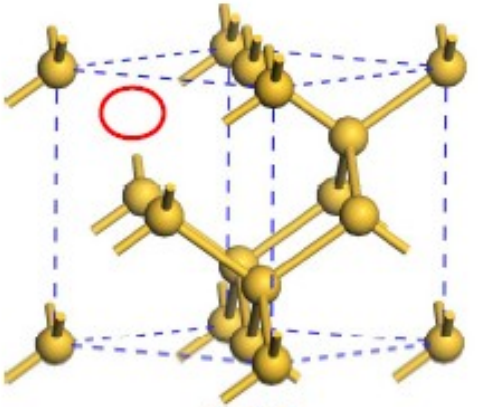




-0.04 eV

-0.10 eV

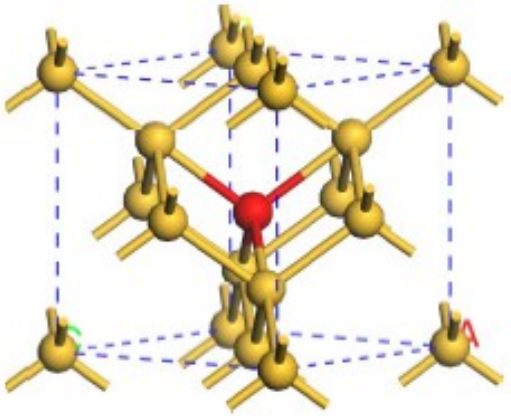




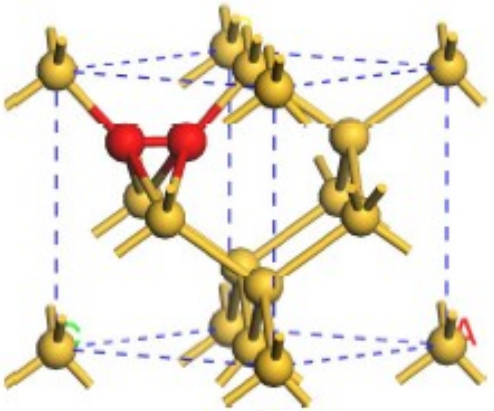
0.23 eV

Formation energy of point defects in silicon: vdW energy contribution

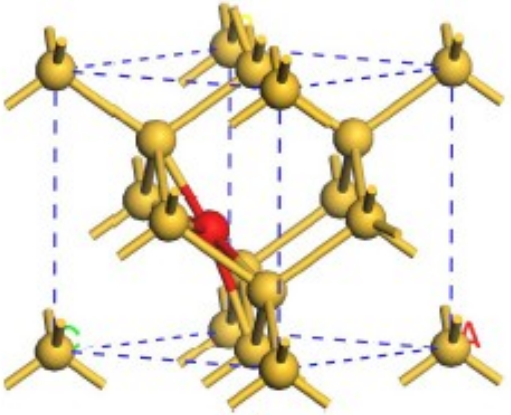
-0.20 eV



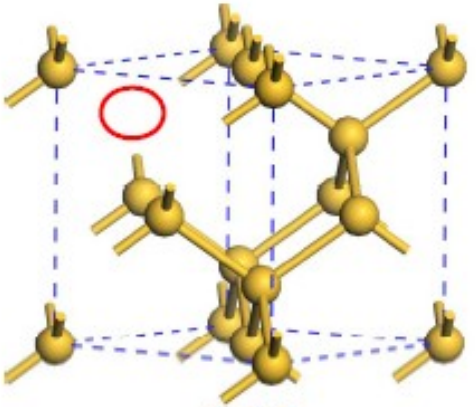
-0.04 eV



-0.10 eV

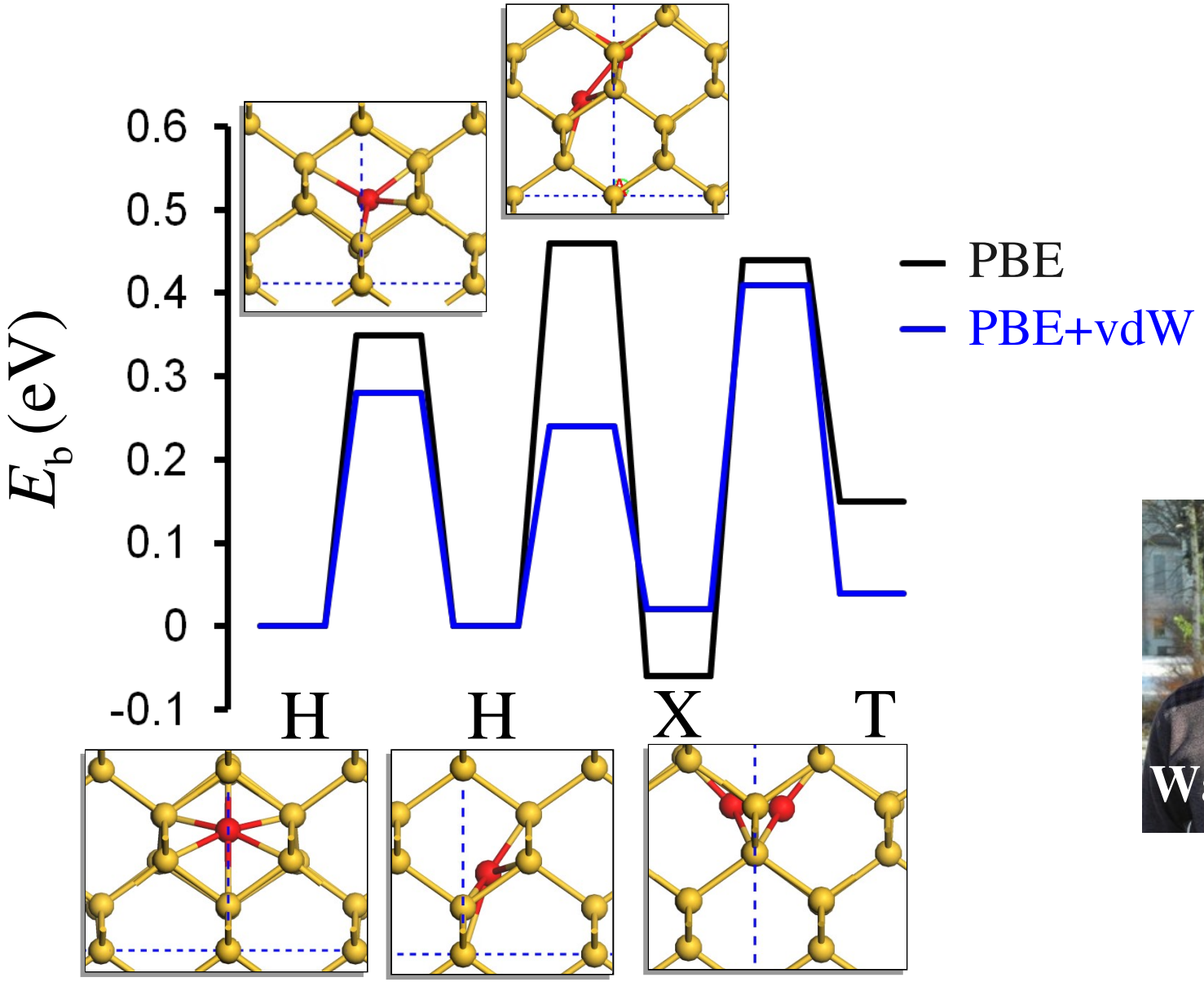


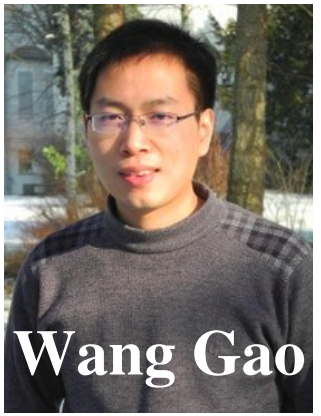
0.23 eV



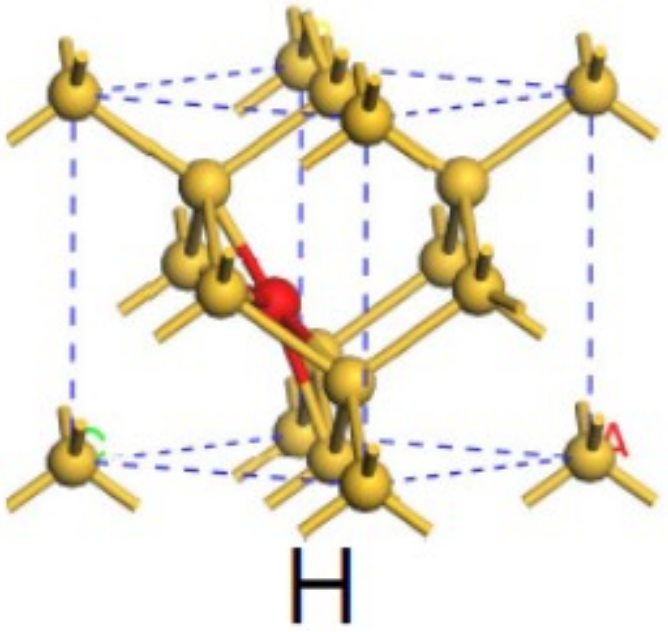
Our HSE+vdW formation energies (~ **4.4 eV** for interstitial and ~ **4.7 eV** for vacancy are in agreement with many-body *GW* calculations and experiments)

Point defects in silicon: vdW interactions change the diffusion mechanism!



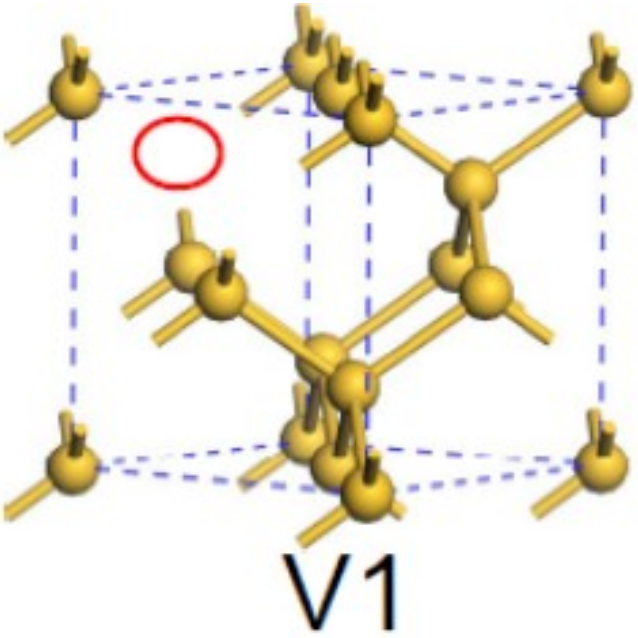


Mechanism for point defect diffusion: *interstitials vs. vacancies*



E_a

?



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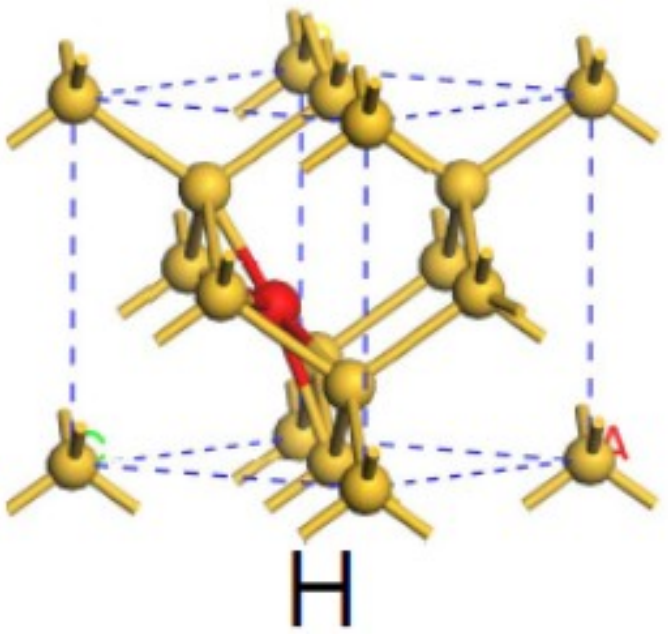
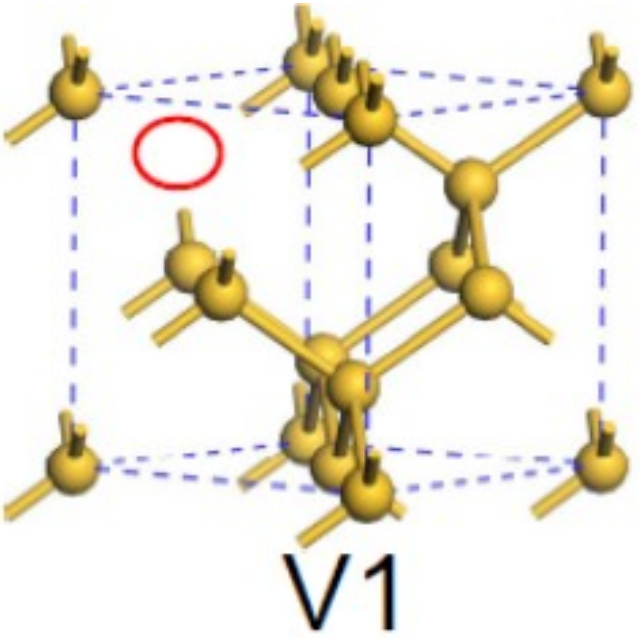


E_a

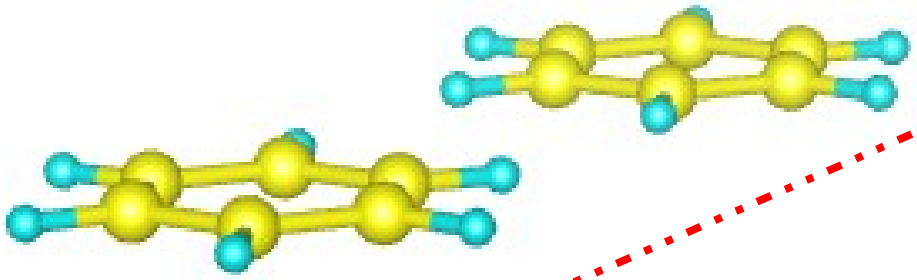
?



	$E_a^{interstitial}$		$E_a^{vacancy}$
HSE	**4.82 eV**	**0.40 eV** →	**5.18 eV**
HSE+vdW	**4.59 eV**	→ **0.93 eV**	**5.52 eV**

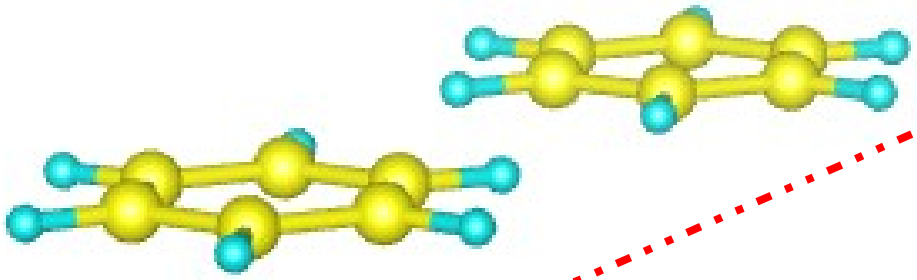
Summary

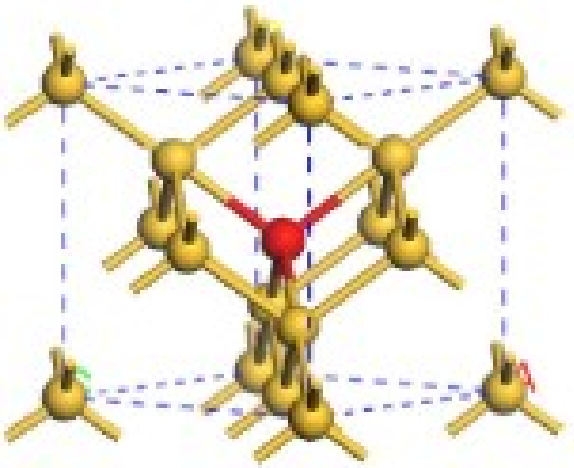
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$



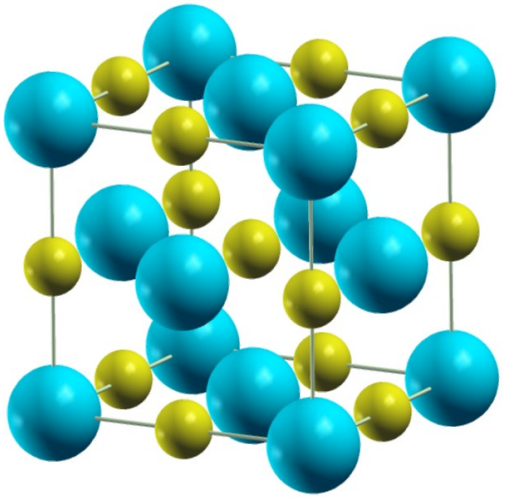
Summary

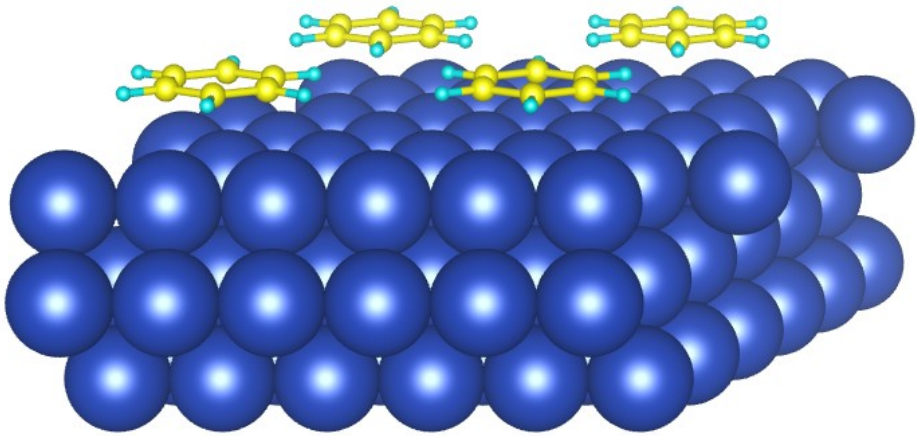
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$



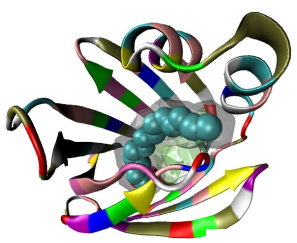


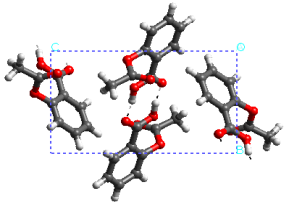
$$\alpha(\mathbf{r};\omega) = \alpha_0(\mathbf{r};\omega) + \alpha_0(\mathbf{r};\omega)\int d\mathbf{r}'\mathcal{T}(\mathbf{r}-\mathbf{r}')\alpha(\mathbf{r}';\omega)$$

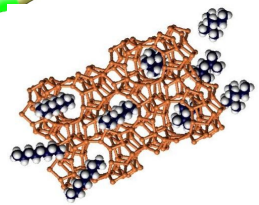




The roadmap to *First-Principles* Description of vdW Interactions in Complex Materials







Screening and many-body vdW energy for finite-gap molecules and solids

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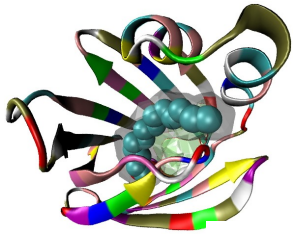
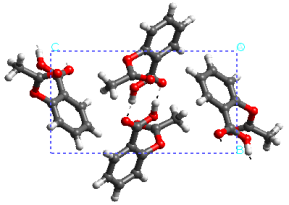
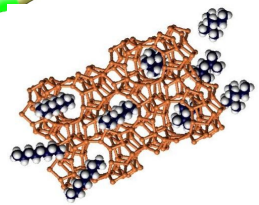


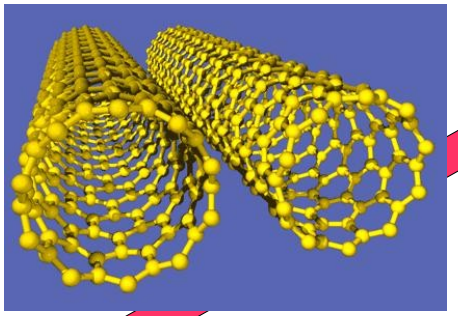




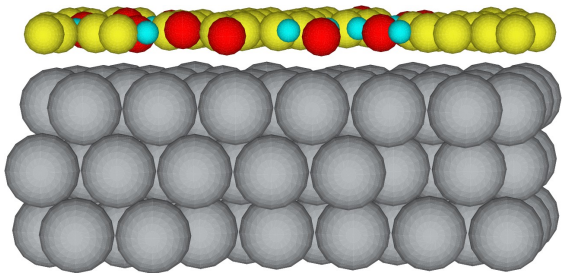
Screening and many-body vdW energy for finite-gap molecules and solids

Higher-order multipole effects; Short-range interaction

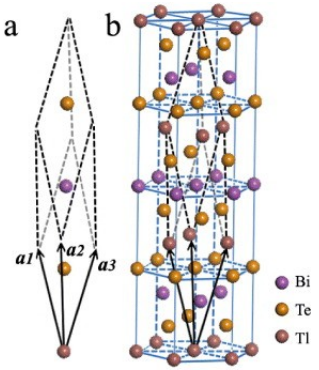
Low-dimensional systems and self-consistency



Hybrid organic/inorganic interfaces



Metallic systems



Ionic systems